# PREFACE

## UNIT PROCESSES AND PRINCIPLES OF CHEMICAL ENGINEERING

The editor's experience of a dozen years in the teaching of this subject has convinced him that modern chemical engineering can successfully be taught only by presenting the main factors of the science in the following logical sequence.

To this end, he has endeavored to develop this book so as to present, (*a*) the fundamental chemical and physical chemical principles which determine the course of any given chemical reaction, (*b*) the so-called unit processes which must be utilized in carrying out the given reaction on a commercial scale, and (*c*) the combination of these processes in their proper sequence and coordination, thus constituting an entire process for the production of the given product.

It is not possible to present and discuss every fact of every unit process within the limits of a moderate sized text-book. A selection must be made so as to include the most important and the most fully studied and developed processes. Back of this selection is the thought that the student will profit more from the thorough study of a few typical and important processes than by getting a smattering of every possible chemical engineering operation. The college graduate is expected to continue his study of the processes with which he must deal in the practise of his vocation, along the lines indicated.

The editor has been fortunate in being able to secure the cooperation of a group of successful practical chemical engineers who have prepared the majority of the chapters in the book. As each man has devoted himself to his own special field the technical information is up-to-date and accurate and it is hoped that whatever differences in method of presentation and point of view which may be found in these chapters will only serve to enrich the subject for the earnest student.

The volume has been prepared primarily for classroom use under the guidance of a competent instructor familiar with present day chemical processes in practice. Problems as well as

a selected bibliography are given in connection with most of the chapters. They may be used together with other supplementary material on both theory and practice. In most cases, students will be given the opportunity of carrying out various operations with some commercial apparatus.

It is the hope of the editor that this volume may be helpful to a great many professors of chemical engineering in the presentation of this vitally important subject, and that it may help to create an enthusiasm for the science in the minds of serious students.

J. C. OLSEN.

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# CONTENTS

# CONTENTS

# CONTENTS

# THE UNIT PROCESSES AND PRINCIPLES OF CHEMICAL ENGINEERING

## INTRODUCTION

JOHN C. OLSEN, Ph.D., D.Sc.

It is advisable, before taking up the study of a given subject, to get as clear a conception as possible of the field covered by the new subject. Chemical engineering includes both chemistry and engineering. Considerable knowledge of the various branches of chemistry, physics and mathematics is an essential prerequisite to the study of chemical engineering.

Engineering has been defined as the science of utilizing the forces and materials of nature and the art of directing human activities for the benefit of man. It is obvious that the activities of the chemical engineer are concerned with the chemical forces and transformation of the materials of nature just as the electrical engineer is primarily concerned with electrical forces. The chemical engineer, in common with other engineers, must be able to direct human effort. All industrial chemical processes must be carried out by many men working under the direction of the chemical engineer. In order to make the enterprise successful, the cooperation of business men, in the capacity of salesmen, directors, and officials of the company, is essential. The chemical engineer must inspire the confidence of these men in himself. In order to succeed in such leadership the chemical engineer must have certain elements of character such as integrity, trust-worthiness and, for the highest success, courage and determination.

The enterprise will not be successful unless it results in "benefit for man." This is ascertained commercially by the "demand" for the product being manufactured. The cost of production must be sufficiently low so that people desiring the product can afford to buy it. For instance, if matches cost five cents or even one cent a piece the sale would be very limited and their use much restricted. By producing matches at one cent for fifty everybody can use them and they become a common, though a great, con-

venience. The chemical engineer and all men engaged in the production of matches are entitled, in return for their work, to a living which is obtained from the profit resulting from the sale of the matches.

Cost of production and the market for his product are therefore important considerations for the chemical engineer. A great deal of his time and thought must be spent in the endeavor to eliminate waste, increase output, and lower the cost of the product. As this greatly increases the sale of the product it generally materially increases the profit. For a number of other reasons many operations are not profitable unless carried out on a sufficiently large scale. This is generally referred to as a "commercial" scale.

As engineering has been very simply defined as applied physics, chemical engineering may be defined as applied physics and chemistry. Various chemical engineering processes require the application of organic, physical, or other branches of chemistry.

Chemical engineering may also be correctly classified as an art. It had been practiced as such long before many of the scientific principles upon which it is based were discovered. For instance, many metals were produced from their ores before our modern conception of the chemical elements and reduction processes even had been suggested. Even today, many processes are developed empirically and explained by scientific principles after it has been shown that a given reaction can be carried out. Many operations are in use which cannot be anticipated or explained scientifically. Many important facts and principles must be learned by experience in a chemical plant and cannot be set forth in a text book on chemical engineering. The student must expect to learn many things when he begins to practice the art of chemical engineering.

A study of various industrial chemical processes will soon show that there are certain operations which are common to many of them. Examples of such operations are grinding, filtration, evaporation, distillation, drying. These are called unit processes. The fundamental scientific principles upon which these operations are based, as well as the apparatus which has been devised to carry out each operation, must be carefully studied. A suitable combination of two or more of these operations in proper sequence and coordination, for the purpose of producing a given product constitutes a chemical engineering process.

As commercial operations must be carried out on a suitably large scale, power must be available for handling the equipment and material. For this purpose electric energy, steam, mechanical power, etc. are available. The chemical engineer must study these sources of power, learning the units of measurement and methods of use of each source of power. He must particularly be familiar with the properties and uses of steam as a source of heat.

In a somewhat broader sense labor may be classed as a source of power, and a study of the organization and direction of human agencies is very important for the chemical engineer. The man who is capable of acting as a leader of men will find such ability of value in the discharge of executive duties which come to the directing engineer.

Plant equipment cannot be constructed of the same material as the chemist employs for his laboratory apparatus. Cheaper and more durable material must be found. Metals such as iron, lead, aluminum, copper, etc., as well as various alloys, and ceramic materials have been found suitable for many types of plant apparatus. The chemical engineer must make a study of these and other materials in order to determine which is most suitable for a given operation. The chemical action on these materials is of the greatest importance both from the standpoint of the durability of the apparatus and the contamination of the material being manufactured.

A careful study must be made of all elements which enter into the cost of a given product. As chemical manufacturing is carried out under competitive conditions and for the purpose of making financial profits the cost of a given product requires accurate analysis. Some of the items which determine the cost of a given product are (a) power, (b) labor, (c) repairs, (d) interest on capital or investment, (e) selling, (f) taxes, (g) raw materials, (h) transportation. The chemical engineer must be continually endeavoring to reduce these and other elements of the cost of his product. Frequently the location of a plant will materially affect the cost. For instance, transportation costs may be reduced if a plant is located near the source of raw material or the market for its product. Plants using a great deal of water must be located near streams or lakes.

In common with all engineering, chemical engineering is fundamentally quantitative and mathematical. Unless the

chemical engineer is able to make the calculations necessary to combine both materials and energy in the proper proportions, as well as properly balance the economic factors involved in the manufacture of the products of the plant, he will not achieve success.    The student is therefore urged not to neglect to solve the problems given at the close of the various chapters.

The chemical reactions involved in a process must be studied in order to be able to carry out a given process in the simplest way and with the least expenditure of labor and energy.    Routine chemical tests must be devised in order to control the course of the reaction, prevent waste and insure the purity of the product. An analytical laboratory must be organized and maintained in connection with most chemical engineering operations.    The development or improvement of a process is carried out by research chemists or chemical engineers who have better training and ability than the chemists who carry out the routine tests for the control of the process after it is in operation.

After the various elementary processes have been studied it is desirable, in a course such as is outlined in this text book, to study a number of well-established commercial chemical industries in order to get a clear understanding of the method of combining the unit operations into a chemical process.    For this purpose such processes as the recovery and purification of glycerine from the soap industry, the recovery of light oil and other by-products from by-product coke ovens, the production of caustic soda and chlorine by the electrolytic decomposition of salt, will be studied. These and other typical chemical engineering processes will be studied because they have been very thoroughly investigated and developed, and a great deal of information is available about them.    It will be impossible, in every case, to present the latest technical development in a given field, because many of these improvements are factory secrets.    Development is also so rapid that neither the author nor printer can keep pace with the forward march of industry.    Fortunately for the illustration of fundamental chemical engineering principles, the latest industrial development is not often necessary.    Many of the processes and principles of chemical engineering have been in use for many decades, and some for centuries.

# CHAPTER I

## HEAT AND POWER

CROSBY FIELD, M.E., M.S. in E.E.

**Introduction.** — Most chemical processes require the addition of heat or the application of mechanical power for successful commercial operation. The design of power-producing equipment is a highly specialized art, properly belonging within the sphere of the mechanical engineer. Its selection and operation in connection with a chemical plant, however, is an important function of the chemical engineer, and one which frequently determines the success or failure of a given chemical plant proposition. This chapter deals, therefore, with the selection and operation of heat and power-producing equipment from the point of view of the chemical engineer, dealing with the theory underlying the design of such units in a brief way, and only insofar as is necessary for the understanding of the essential factors. Power equipment may run into a substantial percentage of the total cost of both installation and operation of the chemical plant, and certain industries, such as the manufacture of aniline dyestuffs, require a variety of power plant equipment rarely found in other industrial plants.

Certain types of power plant processes, such as steam boilers, gas producers, etc., are merely commonplace chemical processes, and the chemical engineer will do well to retain his chemical viewpoint when dealing with them. The power plant, however, can rarely be considered as a separate unit chemical process, because it serves and greatly influences the operation of most, if not all, the chemical equipment in the entire plant.

The availability of a source of heat supply for a given use is largely predetermined by its temperature, although other questions such as the chemical purity of the medium, the rigidity of temperature control required for the process, and other factors also enter. Great economies can often be effected by seeking sources of supply of heat from chemical processes, either exothermic or where heat has been added to cause sublimation or

1

distillation, and afterwards partially recovered in condensers. Under certain conditions it will even pay to collect the heat from sources wherein the temperatures are low, and use it in a step by step increase to a higher temperature. As an example of this latter case, cooling water, after having been warmed by passing through the condensers of a chemical process, has been fed into a feedwater heater and thence into a boiler.

In the last analysis, the success of a chemical engineer depends upon his knowledge of how to produce a new and useful product for which there is a market, or upon his knowledge of how to produce a used product in a cheaper way. By far the greater number of problems fall into the second class, and this knowledge, of course, must be applied to commercial use, either by himself or others, before he can receive financial benefit therefrom. He should, therefore, know where every unit of heat energy in his plant is generated, and where it is consumed. In order to do this he should run a "Heat Balance," as it is called, in which he accounts for all the heat received in his plant, in whatever form it may be, and its ultimate disposal, either as useful or wasted.[1]

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[1] The *heat balance*, as its name implies, is only a convenient way of tabulating the figures showing *quantities of heat*, and is called a "balance" because of its similarity to the bookkeeper's balance sheet. It originated in connection with tests on steam equipment, and became necessary in order properly to determine the performance of the individual units making up the plant under test, such as the boiler, the engine, the condenser, etc. Its application grew until the complete boiler plant and power plant could be examined, and now is quite generally applied to a complete industrial plant. Care must be taken to consider the time-factor, since conditions in a plant change hour by hour, even minute by minute, hence average or representative conditions must be selected. A useful form is:

*Heat Balance—A B Chemical Co., Plant X*
*Winter Operations—Average for October to March*
*Datum Water at Average of 38° F.*

RECEIPTS

| Item | Unit | B.T.U. Unit | No. of Units | Total B.T.U. | Temper- ature |
|------|------|-------------|--------------|--------------|---------------|
| Coal.................. | Ton | 26,000,000 | 2,500 | $65 \times 10^9$ | Room |
| Gas................... | 1000 cu. ft. | 300,000 | | | Room |
| Oil................... | — | — | | | Room |
| Exothermic reaction A..... | — | 3,000 | | | 600° F |
| Exothermic reaction B..... | — | 200 | | | 250° F |
| Hot water, condensers ..... | — | 6,000 | | | 90° F |

Whether the wasted heat is recovered or not is purely a matter of the comparative cost of recovering it and its worth, but whether or not it is ever recovered, it is necessary for the engineer to know how much is being wasted, and whether or not an attempt should be made to recover it. If not useful under present conditions, a sudden change in fuel cost, or a lowering of the price for his product, or the consideration of a proposed cheaper process, may suddenly require a clear and accurate analysis of cost and possible savings, among which the heat saving may be of appreciable magnitude.

In figuring this heat balance, a graphical chart similar to Fig. 1 will frequently be found of great assistance.

EXPENDITURES

| Item | B.T.U. |
|------|--------|
| Product M, (B.T.U. per lb. = 3,000) | 6,700,000 |
| To electricity supplied workmen's homes | 20,000 |
| To mechanical handling of process materials | 116,000 |
| Wastes | — |
| Radiation | — |
| Stack losses | — |
| Process losses | — |
| Loss in electrical transmission | — |
| Unaccounted for | — |

Numerous subdivisions of the above can be made. Make the simple heat balances for each process first, before combining them with the boiler and power plant and then obtain the complete heat balance for the entire plant—you may never need this combined figure. But one figure you will need and should watch every month, that is the total B.T.U. received per pound of product manufactured, and then the cents per pound of product, expended for purchased B.T.U.

The difference between the overall chemical plant heat balance, as outlined above and the heat balance of the boiler plant itself, is shown by the following example from the Babcock & Wilcox Co.'s "Steam" (36th Edition, p. 311, 1927).

| | B.T.U. | Per Cent |
|------|--------|----------|
| Heat absorbed by boiler | 10,791 | 77.08 |
| Loss due to moisture in coal | 25 | 0.18 |
| Loss due to moisture formed in burning $H_2$ | 642 | 4.58 |
| Loss in dry chimney gases | 1,616 | 11.54 |
| Loss due to moisture in air | 39 | 0.28 |
| Loss due to unconsumed C in ash | 323 | 2.31 |
| Loss due to incomplete combustion of C | 227 | 1.62 |
| Radiation and unaccounted losses | 337 | 2.41 |
| Total heat in 1 lb. of coal | 14,000 | 100.00 |

LOW TEMPERATURE
WASTED HEAT

HEAT IN FUEL

A

HEAT RETURNED
TO BOILER

B — FURNACE LOSSES.

C — BOILER LOSSES.

HEAT IN CONDENSATE
FROM PIPES, ETC

D — STACK LOSSES.

E — HIGH PRESSURE
STEAM PIPE LOSSES.

FRICTION LOSSES.

F — PRIME MOVER LOSSES.

EXHAUST
STEAM-HEAT
VALUE

USEFUL POWER FOR
HANDLING MATERIALS,
AGITATION, LIGHTS, ETC

G — LOW PRESSURE
STEAM PIPE LOSSES.

USEFUL MECHANICAL
POWER.

HEAT IN CONDENSATE
FROM JACKETED KETTLES,
ETC.

H — RADIATION FROM
CHEMICAL EQUIPMENT.

J — HEAT IN WATER CARRIED
OUT IN PRODUCTS

HEAT FROM
CONDENSER WATER.

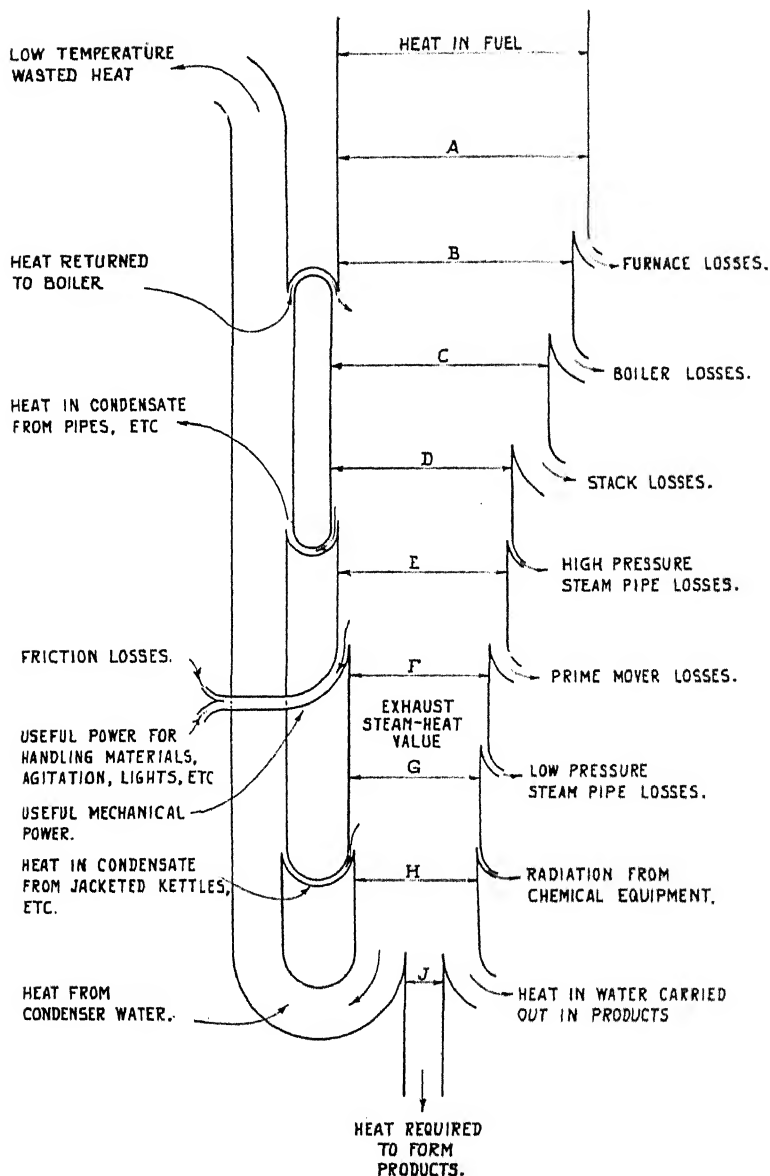HEAT REQUIRED
TO FORM
PRODUCTS.

FIG. 1. Graphic Heat Balance Chart.

**The Steam Boiler Plant.** — The heat power plant which the chemical engineer will most frequently meet is the steam boiler plant in which some form of fuel is burned to generate heat. The heat thus generated is absorbed by water to form steam, and this steam, in turn, is used either to generate mechanical power or to convey its heat into equipment adapted for transfer of the heat from the steam into a chemical process, or both.

The boiler plant itself comprises the boiler including the furnace and some or all of the following accessories or auxiliary equipment:

1. Feed water pumps.
2. Water treaters.
3. Feed water heaters.
4. Evaporators.
5. Economizers.
6. Injectors.
7. Superheaters.
8. Air heaters.
9. Steam accumulators.
10. Steam separators.
11. Mechanical stokers.
12. Pulverizing mills (when powdered fuel is used).
13. Blowers or air compressors (when gas or oil fuel is used).

The term boiler means strictly only that part of the installation through which the heat of combustion is absorbed by the water or steam. Because of the close physical connection involved, the term boiler has been extended to cover as well that part in which the heat is generated, or more properly the furnace.

Fuel is burned in the furnace and part of the heat thus generated is radiated from the mass of burning combustible directly to the metal parts of the boiler and through them into the water and steam. By far the greater part, however, is absorbed by the unburned gases, including the products of combustion, and is carried along by them through passages especially designed so as to bring these gases into close contact with the metal surfaces of the boiler to which they give up a great part of their heat by conduction. Another part of the heat liberated is conducted or radiated to the furnace walls and is by them radiated to the surrounding air. (This seldom exceeds 2 per cent and is even less in modern settings employing water-cooled walls.) That

part of the heat energy ultimately absorbed by the water and steam is considered to be useful energy. The energy radiated through the walls of the boiler setting and that carried off by the gases of combustion from the stack are losses. The latter, however, is by no means a total loss, as it performs a useful function in creating the necessary draft.

The selection of the design of the boiler setting, including the grate area and the dimensions of the gas passages, is largely determined by the kind of fuel to be burned. This varies from waste products of a highly volatile nature, to the hard-to-burn anthracite coal, including specifically pitch, tar, high-volatile bituminous, low-volatile bituminous, lignite and anthracite. In certain other cases oil or gas is used. The leading factors to be borne in mind are, first, that the furnace (or combustion chamber) and the gas passages must have such dimensions that combustion will be complete. The grates must have sufficient area to accommodate the necessary amount of coal or other fuel, and, further, must have a proportion of hole area to surface area great enough to permit the ready passage of the air and yet not permit the coal to drop through into the ash-pit. Where pulverized coal is employed, the furnace volume must be so proportioned as to secure the desired heat liberation per cubic foot and the burners so arranged as to secure the desired turbulence.

Combustion of coal in a furnace is merely a rapid oxidation of a substance partly in the solid phase with an oxidizing agent in the gas phase. The oxidizing agent used is, of course, the oxygen of the air and must be supplied in sufficient quantity and must be properly distributed. The air, containing 23 per cent by weight or 21 per cent by volume of oxygen, is caused to flow through the bed of burning combustible. The force required for this flow, or draft, as it is called, is obtained in one of three ways: first, by the suction draft of the hot chimney gases; second, by a draft mechanically induced by a fan placed between the boiler setting and the chimney; third, by a blower forcing air into the ash-pit underneath the grate (forced draft).

Under certain conditions each of these has its advantages and they are frequently operated in combination, particularly the forced draft and the draft created by the flue gases in the chimney. A combination method that has many advantages is called "balanced draft," in which the air is forced through the fuel bed by a blower at a pressure just sufficient to cause the pressure above

the fuel bed to be atmospheric, and the gases are taken away from the furnace at just the right rate to maintain this condition. Induced draft fans are frequently used instead of the natural chimney draft. Very rarely the natural chimney draft is augmented by a steam jet, but this is expensive to operate. (Jets are more often employed over a stoker to produce turbulence and thus avoid smoke.)

The amount of draft is measured in inches of water,[2] and depends not only upon the fuel being burned and the grate area, but also upon the thickness of the bed and the rate at which the combustible is being burned. This draft may vary anywhere from 0.02 inch up to as high as 2 or 3 inches. In addition to this draft required to force the gas through the bed of the combustible, extra draft is required to force the gas through the passages of the boiler and out through the breeching into the chimney, so that the total draft required is the sum of these three; all of this draft is consumed in overcoming the friction of the fuel and gas passages.

Part of the heat liberated is utilized to heat up the air required for combustion to the temperature of the gases of combustion. In order to lessen the amount of heat thus used, the air may be preheated by heat taken from some other source of the boiler setting where it is not doing useful work. One way of accomplishing this is to have hollow furnace walls and introduce the air to the fuel after passing through the passages in the furnace walls. Another way is to bring the air through a heat exchanger, which permits the air to be heated by the flue gas just before the gas passes into the stack or chimney. The greater the amount of coal burned in a given furnace volume, the higher will be the temperature of the walls of the furnace. In order to prevent the walls from rising to too high a temperature, water pipes covered by a special refractory may be introduced along the sides of the furnace and this heat absorbed to produce steam, at the same time permitting a higher combustion rate without injuring the walls of the furnace. One method of getting an increased burning rate has been to pulverize the fuel and introduce it rapidly underneath the boilers. Pulverized fuel has been rapidly growing in use and real-

[2] "Inches of water," the pressure required to maintain a column of water the given height. Similar to the measurement above and below atmospheric by a column of mercury, and measured in "inches of mercury." One inch of water (at 62° F.) = 0.03609 lb. per square inch = 0.5774 oz. per square inch = 0.0735 in. of mercury (at 62° F.).
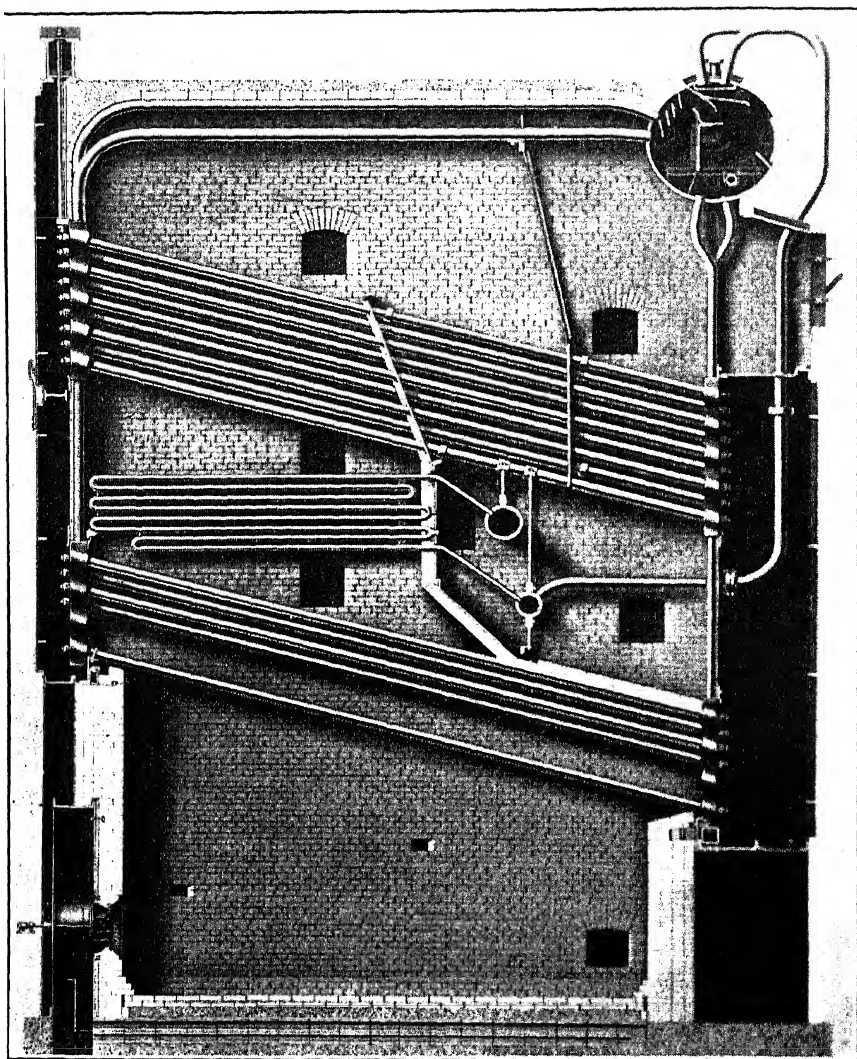
Fig. 2. Water Tube Boiler.

izes high efficiencies. Its introduction, however, must be investi-
gated most carefully before being applied to the specific job on
hand; although it has many advantages, it also has numerous dis-
advantages when considered from the viewpoint of over-all oper-
ating efficiency. Again, local conditions determine the choice,
as under certain conditions the difference in burning rates
between stokers and pulverized coal is small. The latter has
greater flexibility and smaller banking losses, but against this is
the cost of pulverizing and the fact that certain fuels are better
when used on a stoker.

Boilers are generally classified, first, as to where the furnace
is located. If inside the metal structure of the boiler itself it is
called an internally-fired boiler. In an externally-fired boiler,
the most usual stationary type, the furnace is placed below the
boiler proper and the entire equipment is surrounded by a setting
which is generally of brickwork. Examples of the internally-
fired type are the boilers attached to engines used in construction
work, locomotive boilers, and Scotch marine boilers, which will not
be met with ordinarily by the chemical engineer. In the exter-
nally-fired boilers most commonly met, there are fire-tube boilers
in which the furnace gases pass through the tubes of the boiler, the
tubes being surrounded by the water, whereas in water tube
boilers the converse holds true (see Fig. 2). In addition to these
usual types there are sectional boilers composed of small ele-
ments, such as the ordinary cast-iron heating boiler used for
heating homes.

The old method of rating a boiler was an arbitrary matter based
upon no real scientific investigation but arrived at by a standard
of agreement. It had been agreed that a boiler horsepower should
be the heat transfer equivalent to that required to evaporate $34\frac{1}{2}$
lbs. of water from and at 212° F. per hour, and that 10 sq. ft. of
heat absorbing surface equals one boiler horsepower for a water-
tube boiler. It was a rough measure of the heat given to the
water which would be equal to the transfer of 33,524 B.t.u. per
hour. Better practice now tends to rate boilers in terms of
pounds of steam per sq. ft. per hour which the boiler is capable
of evaporating, or, better still, in thousands of B.t.u. absorbed
per sq. ft. per hour, usually expressed as k-B.t.u. per sq. ft. per
hr.

At the time the old standard was adopted, this figure repre-
sented fair operating values. It has not proved a fair value of
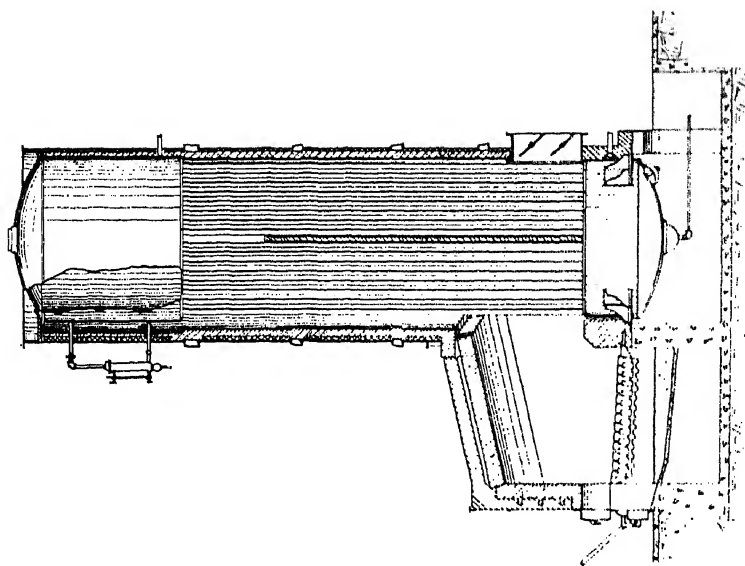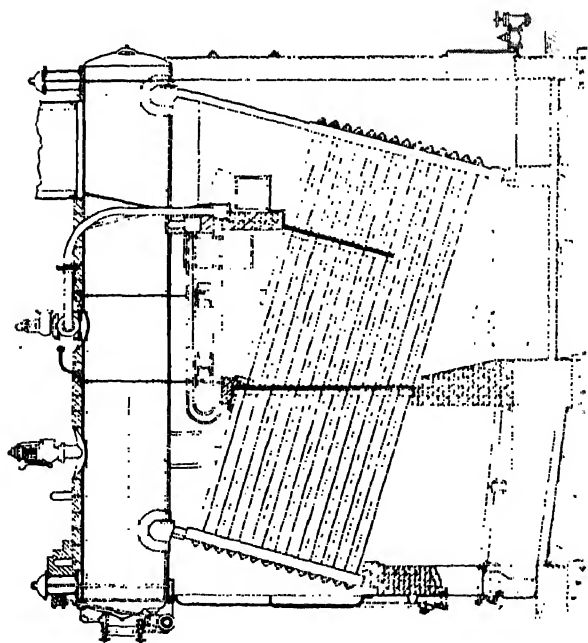
Fig. 4.  Wickes Type Water-Tube Boiler.

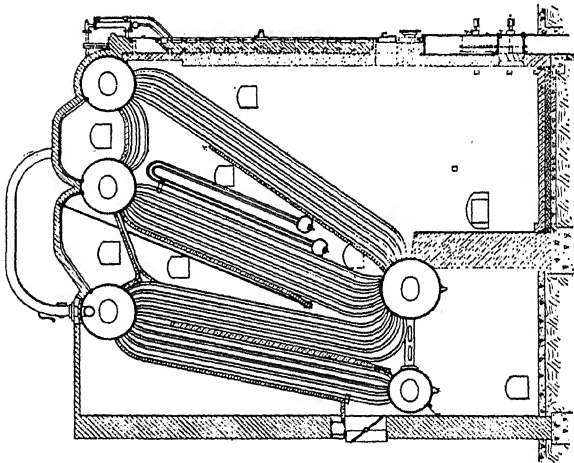Fig. 3.  Box Header, Longitudinal-Drum, 3-Pass Water-Tube Boiler.

Fig. 6. Box-Header, Longitudinal-Drum, Water-Tube Boiler.



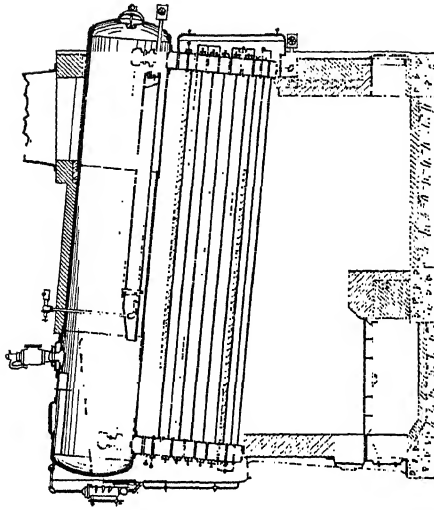Fig. 5. Sterling Type Water-Tube Boiler with Integral Economizer.

the performance of boilers which have been made since that time, however, because of improvements in design and materials. Boilers are now universally run at higher values of performance than their rating at 3,352.4 B.t.u. per sq. ft. per hr. The old expression as a unit of measurement is, however, still used, and that is the reason why you will hear of boilers being run at 200 per cent and even 300 per cent of rating. Just what rating is the most economical for a boiler depends so largely upon operating conditions that a standard rule cannot be laid down. One good rule to follow is so to arrange the boiler plant that when one boiler is out for its periodic overhauling and cleaning the remaining boilers will then not be loaded more than 10 lbs. of steam per sq. ft. per hr., although the more conservative apply this rule to only 8 lbs. of steam per sq. ft. per hr. Under normal conditions of operation, therefore, the boilers will probably run between 4 and 6 lbs. of steam per sq. ft. per hr. This does not, however, provide for much reserve capacity in case large chemical loads are suddenly thrown on the boiler plant. Under these conditions, the boilers must normally operate on a lower percentage of rating in order to have sufficient surplus capacity available for these sudden fluctuations.

In an ordinary fair-sized water-tube boiler plant of say 5,000 sq. ft. of heat-absorbing surface, an over-all efficiency.[3] of 70 per cent is a good average taken over a long period, such as a month. This efficiency may be raised in the larger-sized powdered fuel plants to about 80 per cent. Oil operation would result in an increase of about 2 per cent over operation with ordinary sized coal, and under test conditions for shorter periods powdered fuel efficiencies as high as 90 per cent have been attained.

**Steam Accumulator.** — In order to take care of sudden but not long-continued above-normal demands, the steam accumulator has recently returned to favor in a much improved form. The preferred fluctuation for this installation lasts about one-half hour. The principle of the accumulator is the storing of the heat energy of steam in a large quantity of water, under pressure and at saturation temperature, and releasing this energy in the form of steam under decreasing pressure. R. A. Langworthy gives the chart, Fig. 7, in a paper delivered before the American Society of Mechanical Engineers, December 5–8, 1928. Decision upon

[3] For definition see page 21.

the installation of an accumulator can be reached only after a thorough study of numerous factors of both power plant and load and is a problem for the specialist.
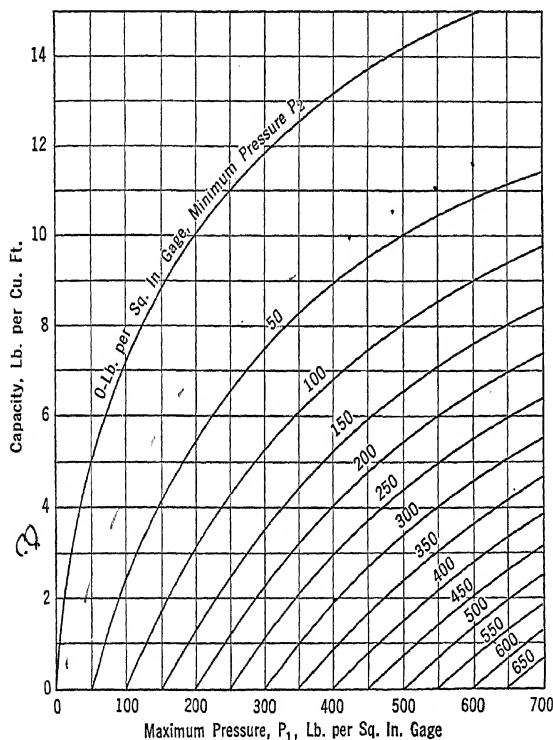


Fig. 7. Curves Showing the Steam-Storage Capacity of Water between any Maximum High Pressure $P_1$ and any Lower Pressure $P_2$.

**Combustion.** — Combustion is purely a chemical reaction between the combustible, or that part of the fuel which can be burned, and air. The heating value of a fuel depends upon the heating value of the elementary contituents of the combustible such as carbon, hydrogen, etc. The heating values of the combustibles ordinarily met with in fuels together with other data of interest in connection with combustion are given in the following table.

| | Higher Heat value, B.T.U. per Lb. | Lbs. Air per Lb of Combustible |
|---|---|---|
| Fixed carbon to carbon monoxide (CO) (Incomplete combustion) | 4,351 | 5.76 |
| Carbon monoxide to carbon dioxide (CO$_2$) | 10,193 | 2.45 |
| Fixed carbon to carbon dioxide (Complete combustion) | 14,544 | 11.52 |
| Hydrogen to water (H$_2$O) | 61,040 | 34.56 |
| Methane (CH$_4$) to carbon dioxide and water | 23,900 | 17.28 |
| Sulfur to sulfur dioxide | 3,890 | |
| Olefiant gas (C$_2$H$_4$) to carbon dioxide and water | 21,320 | 14.81 |
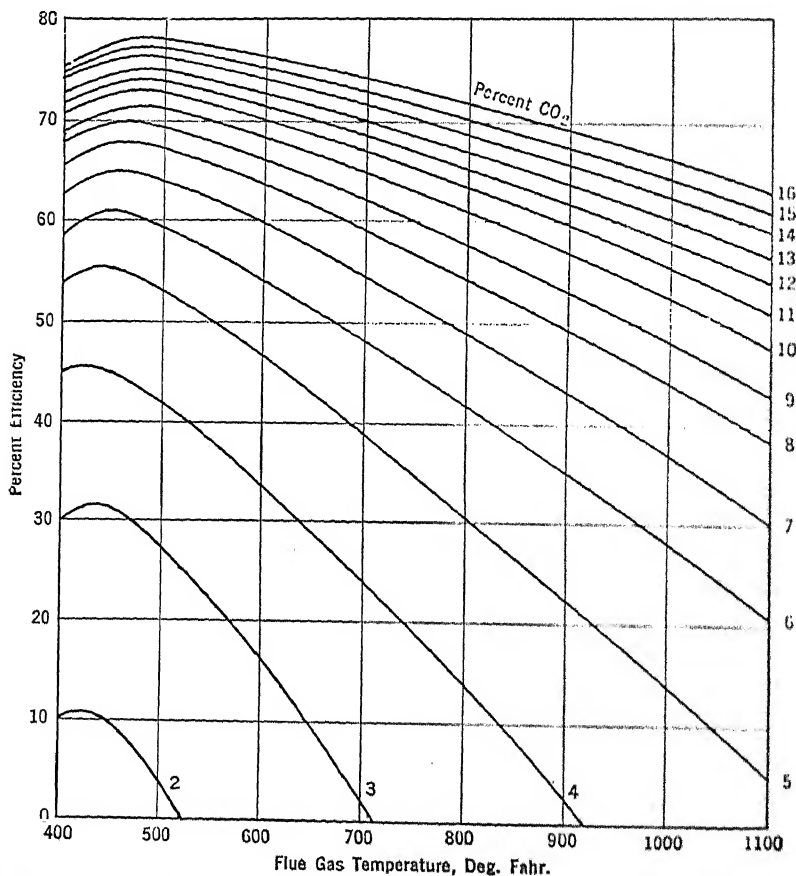


FIG. 8.   Boiler Efficiency as Related to Per Cent CO$_2$ and Flue Gas Temperature.

The theoretical air given in the last column cannot be used in practical operation, due to several factors, but principally to the impossibility of getting the limited amount of air into contact with all the burning surfaces of the fuel. It is necessary, therefore, to force into the furnace an excess of air, varying from 15 per cent to 75 per cent more than that theoretically required for the combustion. This excess air causes a loss of heat, but a small amount performs a useful purpose in keeping down the temperature within the furnace to a point which prevents the fusion of the furnace walls and ash, which would result in clinkers and excessive maintenance of brickwork.

|  | *Temperatures Attained* | |
|---|---|---|
|  | *Theoretical Air* | *100% Excess* |
| Carbon to $CO_2$ | 4952° F. | 2283° F. |
| Carbon to CO | 2666° F. | 1304° F. |
| CO to $CO_2$ | 4475° F. | 2861° F. |
| Hydrogen | 4010° F. | 2459° F. |
| Sulfur | 3571° F. | 1655° F. |

Theoretically, with pure carbon as the fuel, the highest possible percentage of $CO_2$ in the flue gases (by volume) is 21 per cent,
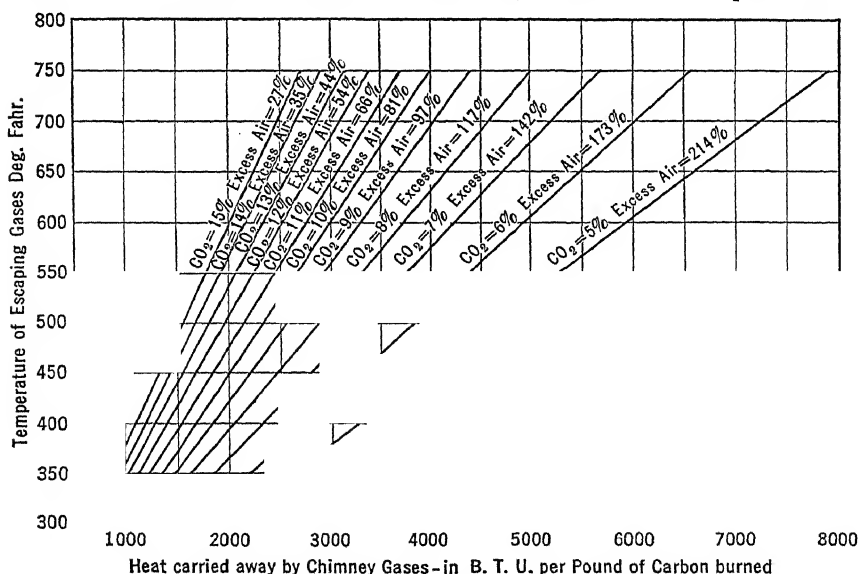


FIG. 9. Loss Due to Heat Carried Away by Chimney Gases for Varying Percentages of Carbon Dioxide. Based on Boiler Room Temperature = 80 Degrees Fahrenheit. Nitrogen in Flue Gas = 80.5 Per Cent. Carbon Monoxide in Flue Gas = 0 Per Cent.

which assumes the 21 per cent oxygen burned to 21 per cent $CO_2$. The 79 per cent nitrogen (inert gas) takes no part in the combustion, but does act as a carrier of heat. The temperature in the furnace, before the hot gases have given up any of their sensible heat to the furnace walls or the heat absorbing surface of the boiler, may be calculated by the percentage of carbon dioxide in the flue gas. Figs. 8 and 9 are of much use in practical work, and though approximate, will be found very useful for quick checking of operating conditions in the plant. They are also useful for day by day comparison of operating boiler room shifts.

*Example.* — If a thermometer in the flue breeching reads 550° F. at the same time that a carbon dioxide meter indicates 10 per
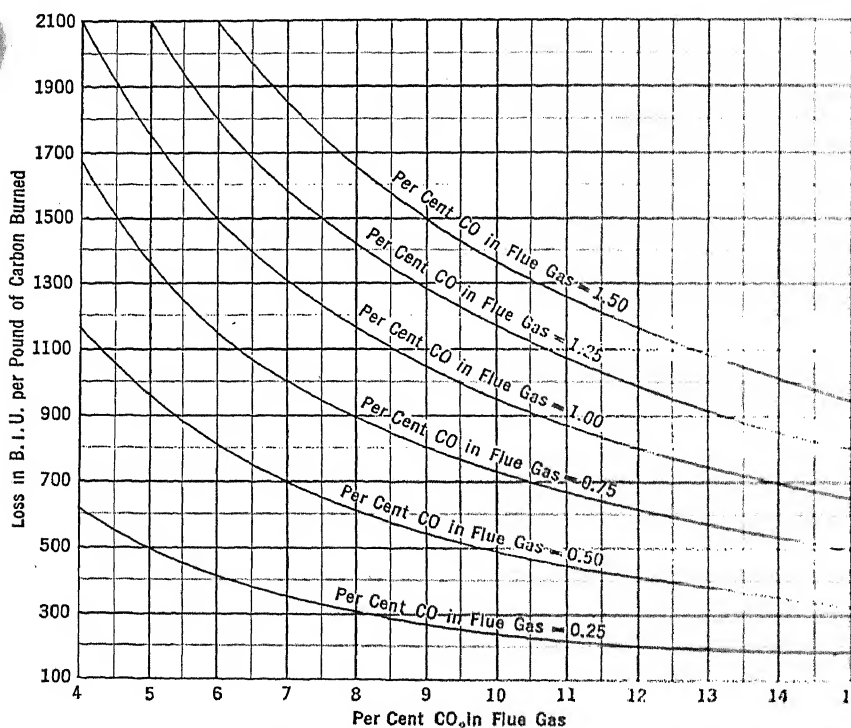


Fig. 10.    Loss of Heat in Flue Gases Dependent Upon Percentage of $CO_2$ and CO.

cent (with no carbon monoxide), then Fig. 8 above shows the boiler is operating at an over-all efficiency of 70 per cent. Fig. 9 shows that under these conditions (of 81 per cent excess air) 2670 B.t.u. is carried away by the chimney gases for each pound of carbon burned.

Fig. 10 shows a refinement in calculation to be made whenever there is carbon monoxide present. Although much better conditions are obtainable in large boiler houses, yet in the average plant a carbon dioxide percentage of 10 to 14, accompanied by a flue gas temperature of 550° to 650° F., is considered good, below that, poor, and above that, excellent.

The temperature required for the ignition of the fuel, known as the "kindling temperature," varies greatly with the concentration, the fineness of solid particles, the pressure and the presence or absence of catalysts. Under normal boiler operating conditions the kindling temperature of the fixed carbon in bituminous coal is about 750° F., in anthracite coal about 925° F., for hydrogen 1090° F., and carbon monoxide 1210° F.

**Fuels.** — In addition to the combustible in a fuel, there may be certain non-burnable constituents. A proximate analysis of coal gives four constituents, two burnable and two non-burnable. These are:

1. Fixed carbon (or coke).
2. Volatile matter (including tar). } Combustible
3. Ash.
4. Water. } Non-burnable

The heating value of coals, therefore, varies greatly, depending upon the relative amounts of the various combustibles. Thus, on an "as delivered" basis, including ash and moisture, anthracite coal will run about 12,500 to 13,350 B.t.u. per lb.; semi-bituminous about 14,000 to 14,700 B.t.u. per lb.; bituminous from 10,900 to 14,100 B.t.u. per lb.

An analysis reporting the fixed carbon, volatile matter, ash and water is called a *proximate* analysis and gives all the information usually necessary for operation of boiler plants. Should a further study be desired, then an *ultimate* analysis is required, which gives the amount of all the elements in the fuel, such as carbon, hydrogen, oxygen, nitrogen, sulfur, moisture, and ash.

All liquid fuels must be thoroughly investigated before use as

to the best method of handling and burning, as they vary greatly.
Properties of particular importance are the flash-point (the tem-
perature at which the inflammable vapor given off will ignite
temporarily); the fire-point (the temperature of ignition and
continued burning); the viscosity, and the percentage (if any)
which forms an explosive mixture with air.   The handling during
cold weather of the heavier oils presents a problem, requiring
steam coils both in the tank cars and the storage tanks to reduce
the viscosity sufficiently to permit the oil to flow.

**Grates and Burners.** — Pulverized coal is carried into the fur-
nace in a stream of air, so that its burning partakes more of the
nature of burning a fluid than a solid.   This same condition
applies to "colloidal" fuel, which is a mixture of fuel oil and solid
particles of finely ground coal or coke, and may be burned with
the ordinary fuel oil burning equipment.   Its heating value is
from 16,500 to 17,500 B.t.u. per pound.   It is not yet much
used in the United States, in spite of its apparent advantages in
its ability to utilize otherwise unusable grades of coal, coke breeze,
etc.   It is not unlikely that the rapid advance in the use of pul-
verized coal equipment will still further limit its field of appli-
cation.

In order to burn solid fuels, some sort of grate must be pro-
vided, which performs the following functions:

(*a*) Supports the fuel while being brought up to the ignition tem-
       perature and thereafter while burning.
(*b*) Distributes the air uniformly to the fuel.
(*c*) Separates out the burned ash, and sometimes
(*d*) Feeds and distributes fresh fuel automatically, in performing
       which function the grate becomes an automatic stoker.

The grate may be either stationary or shaking.   The dif-
ficulties in stoking a furnace with stationary grates are so
tremendous that their use is very limited.   Shaking grates are
so arranged that usually by means of a rocking mechanism the
bars can be oscillated sufficiently to throw down the ashes and
even to dump the fire by means of a handle outside.   A grate is
built up of bars of various shapes, through which there are holes
to permit the passage of air and ash.   They vary from quarter-
inch diameter round holes for burning saw-dust to slots one inch

wide by several inches long for burning the largest commercial anthracite lumps.

Hand firing is found to be inefficient, if for no other reason than that efficiency can be maintained only by uniformity of efficient conditions; and this uniformity within a furnace is constantly being changed by the periodic opening of the fire doors to feed fresh fuel. Because of this and other obvious conditions, as soon as the boiler becomes of a size sufficient to make a few per cent of inefficiency amount to something annually in dollars and cents, automatic stokers should be installed. Just what this size is depends upon local conditions, but ordinarily will be found to be between 2,500 and 5,000 sq. ft. of heat absorbing surface. Recently many small stokers have been sold for boilers as small as 1,000 sq. ft., particularly where smoke prevention ordinances have been enforced.

A type of furnace that is now coming into general use because of the high ratings, high efficiencies and flexibility, is designed to burn coal in pulverized form. One popular form of handling the ash is to have it fall into a hopper which is emptied at intervals into a sluicing trough having water jets which carry it away to a dump or fill. Another method is to empty the ash into a trough which forms a part of an ash-ejector system or it may be wet down and emptied into hand cars or trucks and disposed of as desired. Still another form which is becoming popular among the larger plants is the slag-type furnace, in which the ash is maintained in molten form in a well at the bottom of the furnace. This molten slag is tapped periodically into a sluicing system for disposal. In any case, only about 20 or 30 per cent of the ash finds its way to the bottom of the furnace; the rest goes out with the stack gases and mingles with the atmosphere.

The principal liquid fuel is petroleum oil. It is stored in tanks, and for safety must always be pumped to the furnace and never flow to it by gravity. The oil must be completely atomized, thoroughly mixed with the right proportion of air for combustion, and be burned in a furnace having ample volume. There are two general types of burners: the mechanical in which the atomizing is done by the oil itself as it issues under pressure from the supply pipe through a specially formed tip which breaks it up into fine particles, and the spray type of burner which mixes the liquid with a jet of compressed air or steam and forces it into the furnace.

HIGHER HEATING VALUES, IN B.T.U. PER LB. OF VARIOUS LIQUID FUELS

California fuel oils.................................. 18,000–21,000
Gasoline........................................... 19,980–20,520
Kerosene........................................... 18,625–20,160
Ethyl alcohol (Denatured).......................... 11,000–11,750

*Gas Fuel.* — The ideal fuel is of course gas, but the cost is usually prohibitive for power boilers except in a natural gas district. For chemical processes, where accuracy of temperature control is required, it frequently pays to install a producer gas plant, but this is rarely the case for power boilers. With gas, there is of course no grate required, but as with oil, there must be provided some form of special burner for mixing the correct proportions of gas and air and injecting them into the furnace; also some refractory brick work maintained by the flame at a temperature hot enough to ignite the fresh fuel-air mixture, and furnaces of ample volume.

The use of producer gas fuel for stills, autoclaves and other reaction-vessels, where accuracy of temperature control is required, is so preferable to oil or coal that it should always be investigated, and for that reason the gas producer is mentioned in more detail here. The producer has for its object the conversion of a solid fuel into gas. In accomplishing this, air or an air-steam mixture is blown through a relatively thick layer of incandescent fuel. New fuel is added continuously above this layer, and the residue, principally ash, is continuously removed from the bottom.

The producer itself consists of a steel shell, lined sides and top with fire brick, and is sometimes water cooled. It is usually circular in section, with proper grates in the bottom. A blower to suck the gas from the producer and force it through the distributing pipe lines, and a scrubber to cool the gas and clean it of tar are also required to complete the installation. Producers using bituminous coal must be mechanically agitated, which is not necessary in those using anthracite.

The gas made depends, of course, upon the nature of the fuel and the operating conditions, but the combustible portion consists mainly of carbon monoxide, which will be from 20 per cent to 30 per cent of the total gas volume; hydrogen and methane follow; the former may be from 10 per cent to 20 per cent, the latter under 5 per cent. In addition to the inert nitrogen from

the air, which forms about half of the total gas volume, some carbon dioxide is made. This may vary from 2 per cent to 20 per cent of the total gas volume.

HIGHER HEATING VALUES OF PRINCIPAL GAS FUELS IN B.T.U. PER CUBIC FOOT
(AT 760 MM. PRESSURE AND 60° F.)

Natural gas............................................. 950–1500
Illuminating gas........................................ 450– 600
Producer gas........................................... 120– 160
Acetylene..............................................1475–1590
Blast furnace gas....................................... 80– 100
Coke oven gas.......................................... 500– 650

The selection of the proper fuel depends entirely upon local conditions, and in ascertaining the cheapest, not only must the delivered cost be considered, but, also the labor of handling (including ashes in the case of coal) and the fixed charges on the investment. The fuel selected for the chemical process may not be the same as that for the boiler plant, because in the former case questions of accurate control of temperature may be all-important, whereas boiler plant equipment has been so well developed that much wider limits in choice of fuel are permissible.

The only real test of the efficiency of operation of a boiler is the "yield" of useful B.t.u. in the steam as compared with the B.t.u. in the fuel as fired, commonly called the "Combined Furnace and Boiler Efficiency" or the "Over-all Efficiency." This value is obtained over short periods, say every hour, as would be necessary in the daily operation of the boiler, particularly where the load is subject to fluctuation. All of the values obtained for a large number of consecutive periods, say a week or a month, are averaged for the final value.

It is not easy, however, to obtain a true yield figure. One of the easier methods of control is to analyze the flue gases with a continuous carbon dioxide recorder, or from time to time with a portable Orsat set. By means of this equipment the percentage carbon dioxide in the flue gas can be obtained rapidly, which figure, combined with the record of flue gas temperature, gives an index of operation quite closely in accord with the true yield.[4]

**Boiler Accessories.** — Although the boiler and furnace together are the main parts of a boiler plant, a great deal depends

[4] See Curves, page 14.

upon the accessories.    We have already discussed the principal accessories of the furnace, having omitted the purely mechanical coal and ash handling equipment and now come to those more
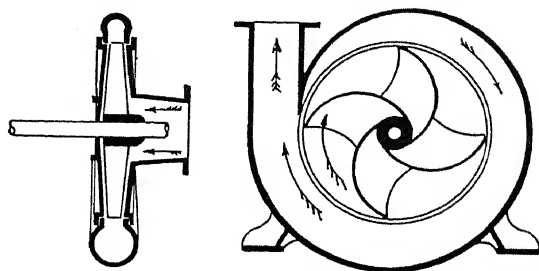


Fig. 11.    One-Stage Centrifugal Pump with Volute Casing.

closely a part of the boiler.    First, some method of getting the water into the boiler is necessary and this is usually accomplished by means of feed water pumps, although in the smaller-sized plants injectors are still used.[5]    Feed water pumps are usually
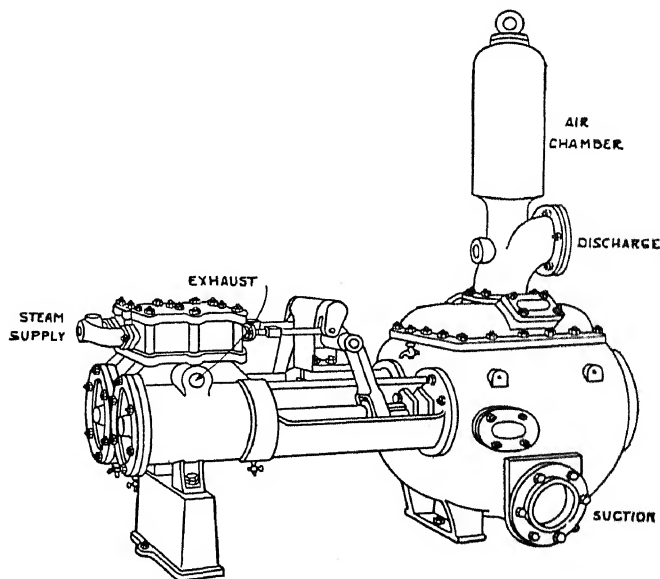


Fig. 12.    Duplex Pump.

[5] Figures 11, 12, 13 illustrate briefly the four different types of pumps used to feed boilers.    Only the simplest form of centrifugal pump is shown, as it illustrates

duplex steam pumps, although centrifugal pumps, either motor
or turbine-driven, are being more and more generally used.
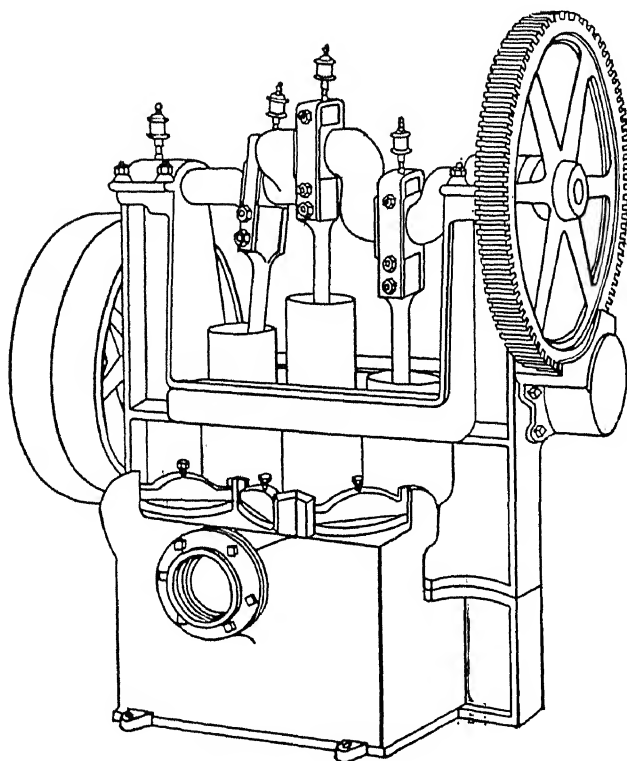


FIG. 13. Triplex Pump.
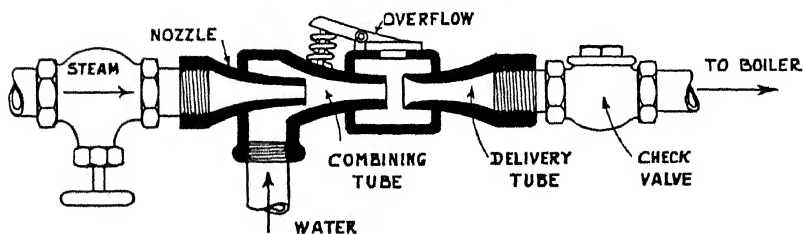


FIG. 14. Steam Injector.

the principle best, although this type of rotor could rarely be used for high pres-
sures. The operation of the duplex pump and the triplex pump and their many
modifications are given in handbooks and in other mechanical engineering treatises.

There are also a few motor-driven triplex pumps used. The exhaust from steam-driven pumps is of course utilized to heat the feed water.

One of the most interesting problems from the viewpoint of the chemical engineer is that of the chemistry of boiler feed water. One fact must never be lost sight of; the boiler is an apparatus for heat transfer, not a piece of chemical equipment for chemical reactions. Feed water is usually treated in separate equipment. In the past this has been done by treatment with chemicals specifically selected for the particular water being used, and usually took the form of large water softening equipment. Distilled water is being used more and more. At first this practice was introduced into central stations, where the steam was condensed and then re-used, so that the evaporator had to supply only make-up water; but it is coming into use more and more in chemical plants, where practically all the boiler feed water is consumed in the form of process steam, either directly from the boiler, or after passing through the turbines.

As the steam comes from the boiler it is presumably dry and saturated,[6] but before it proceeds any great distance in the pipe, its contact with the surface of the pipe causes it to give up some

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Injectors are also frequently installed in the larger plants as a reserve for emergency use, in case of failure of the pumps. The principle of the injector is shown in the Fig. 14. High-pressure steam from the boiler acquires a high velocity in passing through the nozzle, and is condensed by the water in the combining tube, creating a vacuum into which the water from the supply pipe is sucked. This mixture of condensed steam and water is forced by the high velocity steam into pressure head, which lifts the check valve and the (now) hot water enters the boiler.

From the viewpoint of the mechanical work of pumping water into the boiler, the injector has a very low efficiency; but inasmuch as practically all the heat in the original steam is carried back into the boiler, its thermal efficiency is nearly 100 per cent.

[6] Briefly, steam is pure water vapor, at any pressure, whether above or below atmospheric. It is handled commercially in the following: Saturated steam, when its temperature is that corresponding to its pressure—not superheated. Superheated steam is steam heated to a temperature above that corresponding to its pressure. When the steam contains no liquid water, it is said to be dry, and dry steam may be either saturated or superheated. Wet steam is steam containing water, in the form of "slugs," globules, spray or mist. The temperature of saturated steam is that due to its own pressure; if air or other gases be present this pressure is proportionately less than the total pressure measured by the gage. Quality, or the quality factor, expresses the proportion of true saturated vapor there is present in terms of the total mixture. Thus, if the quality be 85 per cent, 85 per cent of every pound of mixture is vapor and 15 per cent is liquid.

of its heat which results in a condensation of part of the steam into water. As the steam piping in a chemical plant is normally long, there will be an abnormal amount of condensation, so that the steam will be quite wet by the time it approaches the point of utilization. In order to avoid this, steam is superheated by being passed through pipes which lie in the furnace gas passages and thus raise the temperature of the steam above the normal temperature of the steam for this pressure. Superheated steam has a further advantage in that it will not give up its heat so rapidly to the surface of the pipe as will saturated steam.[7] Further, engines and turbines operate with greater economy with superheat, consequently, if the steam from the boiler plant is to be utilized first in turbines or engines, it is advantageous to have it superheated.

The temperature of the flue gases in the chimney may be as low as 300 or 400° F., although a normal temperature is somewhere around 550° F. In either case it is too low to cause much flow of heat from the gases into additional sections of the boiler. In order to make use of the heat in these gases, feed water is heated by passing it through tubes which are surrounded by the hot flue gases. The apparatus is called an economizer. Cast iron instead of steel was formerly used as it is not as susceptible to the action of oxygen in the water; where the water is deaerated, steel economizers are commonly used. The economizer is placed upon the discharge side of the feed water pumps. In taking up this additional heat, however, the draft is seriously interfered with and additional load is thrown upon the fans and other mechanical equipment. The cost of the economizer is by no means low, and the installation cost should always be compared with the savings made possible by its use. A great many engineers in chemical plants much prefer to put the money into a greater amount of boiler surface which they feel will afford them greater reserve capacity. Another competitor of the economizer for any surplus heat which it may be practical to extract from the flue gases without too much interference with the draft is the *air heater*, for preheating the air entering the furnace. This is a development in this country of the past few years, and is itself a matter for special study.

*Feed Water Heaters.* — It would be unsatisfactory to feed

[7] See chapter on Heat Transfer; it will be noted that $K$ for condensing vapor is many times $K$ for gas.

cold water directly into the boiler. It would set up temperature strains, and would interfere with proper circulation. More incrustation due to precipitation of salts and more corrosion due to aeration would also result. There is also some condensate usually available from pipes or engines, and in spite of all efforts to use it in process, yet at times there will be a quantity of exhaust steam to use. For these reasons the cold water is preheated in a feed water heater, of which there are two general types, closed heaters and open heaters. (The economizer is sometimes considered a third type.) In the open heater the heating medium and the water mix; in the closed they are kept separate by flowing one or the other through tubes. The latter is more expensive to install and not quite so efficient, but has the advantage of keeping out of the boiler any oil or other impurity in the exhaust steam or condensate.

**Power Steam.** — Steam manufactured in the boiler is destined for use in one of two ways: first, to furnish heat to assist in a chemical endothermic reaction, or other heat absorption operation, such as drying, heating, or evaporating; secondly, to convert its heat content into another form of energy. The first is generally called "Process Steam," and the second "Power Steam." The use of "Process Steam" will be discussed in Subsequent Chapters.

The principal uses of power steam are for conversion into:

(*a*) Mechanical Energy; converted by some form of steam engine or turbine and made available for such purposes as driving autoclave agitators, grinders, elevating machinery, or the like.

(*b*) Electrical Energy; for one of four purposes:
1. Operation of electrochemical processes; such as electrolysis.
2. Electric heating.
3. Electric light.
4. For transmission and more convenient retransformation back into mechanical energy by means of electric motors for same uses as (*a*).

(*c*) Compressed Gases (usually air).
1. For air agitation.
2. For drying, as in filter press work.

3. For transporting chemicals under pressure, as in acid eggs or air conveying and separating.
4. For sand blasting.
5. For compressor type refrigerating machinery.
6. For transmission and reconversion into mechanical energy, as in air hoists, thus being in competition with (*b*-4), above.
7. For conveying of heat or moisture.
8. For ventilating, including carrying off of fumes, etc.
9. For atomizing, as in fuel oil burners.

(*d*) Hydraulic Energy; such as water or other liquid pumps.
(*e*) Refrigeration (by means of the absorption system).

Note that most, although not all, applications of *c*, *d*, and *e*, call for conversion to mechanical energy first, and then immediate reconversion to another form. It becomes a real problem to decide the location in the plant of the various conversions, whether the conversions from steam to the other form shall be done at a point near the boilers, and distributed through multiple transmission systems of steam (high and low pressure; exhaust or bleeder), electricity, compressed air, ammonia, brine, water, etc., or whether high-pressure steam alone shall be transmitted and, near the point of use, converted into as many of the other forms as necessary.

The normal, although not universal, practice is to group all the conversion equipment in one location called the engine room, where it will be reasonably well protected from the effects of the chemicals and where it can be tended by a minimum number of trained operators. Usually the engine room is near the boiler plant, and both as near the center of the manufacturing operations as fuel and ash handling will permit. This normally requires the use of electric motors at other points where mechanical energy is required.

The selection of the proper boiler pressure is determined by the relative power and process steam demands, and the highest process temperature, with an allowance for temperature loss as the heat is transmitted through pipes.

The balance between the Process Steam and the Power Steam is one of the most puzzling yet most necessary problems to be met with in practical plant operation. In making such a study the time-schedule of each chemical unit process must be inves-

tigated. It is frequently good policy to change the chemical operation time schedule in order to balance the plant. This is too complicated a problem to discuss more fully here.[8]

**Engines and Turbines.** — Steam is converted into mechanical energy, by means of a reciprocating piston type of steam engine, or by a turbine. Reciprocating steam engines are classified in various ways, depending upon what particular feature of their construction or operation is under discussion. As a rule, single-acting are found only in small sizes, 20 H.P. or less, although recently large single-acting engines are being developed for special cases such as the 6000 H.P. engines at 1450 pounds pressure at the new Phillip-Carey plant. The chemical engineer will usually meet horizontal, double-acting engines, 200 H.P. or less in size.

A further classification is according to the method of operation. Thus the engine may be run either non-condensing, exhausting its steam into the atmosphere or into a receiver above atmospheric pressure; or it may be run condensing, exhausting into a receiver in which the pressure is always maintained less than atmospheric by causing the steam to condense into water by abstracting its heat by cold water. Air and other non-condensing gases are always caught in such a system, so in addition to the water supplied, some form of air pump must be attached to the condenser to remove them. In still a third method of operation the steam is extracted or "bled" from the engine at a pressure greater than that at which the main flow of steam is exhausted. "Bleeder" type engines are usually compound, and the steam is taken from an intermediate receiver, placed between two of the stages.

There are many types of steam turbines, but in general they fall into one of two general classes, or into a mixed type which combines features of both. The principle of the turbine is the conversion of the available heat energy of the steam into kinetic

[8] For a discussion of this subject reference may be had to the author's "Exhaust Steam at High Back Pressures" (Chem. & Met. Eng., Jan. 1st, 1919), "Some Odd Applications of Steam" (Chem. & Met. Eng., **34**, Nos. 9 and 10, Sept. and Oct., 1927), "Tests on Small Engines at High Back Pressures" (with A. E. Flowers & R. J. Peffer, Chem. & Met. Eng., Feb. 18, 1920) and R. V. Kleinschmidt's "Balancing Heat and Power in Industrial Plants," presented before the American Society of Mechanical Engineers, December 5–7, 1928. Note that there is at present a marked tendency toward steam pressures at 400 lbs. or higher, then exhausting through turbines to the desired process pressure.

energy by its expansion in a suitably designed passage, resulting
in the issuance of the steam from this passage in the form of a
jet.   If this expansion takes place in a fixed nozzle, and upon
issuing from this nozzle the jet strikes curved blades upon a
revolving disc and to them imparts mechanical energy, the turbine
is called an impulse turbine.   If on the other hand, the expansion
takes place in the moveable channel, so that the reaction of the
jet itself causes the rotation, the turbine is called a reaction
turbine.   Some designs use both impulse and reaction features.
   The subject of turbines is, of course, extensive, as there are
many classes and kinds, but the fundamental principle of the
multi-stage type is shown in Fig. 15.   The entering steam ex-
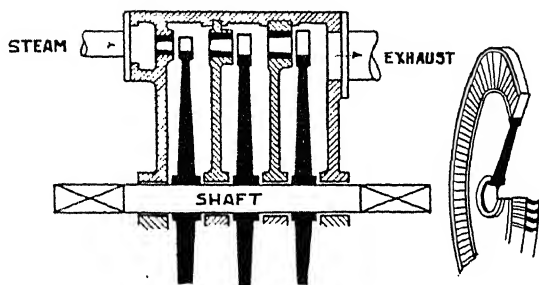


Fig. 15.   Steam Turbine.

pands through the first ring of nozzles acquiring a relatively low
velocity and discharges against the buckets in the first stage
casing, where the pressure is somewhat lower than the inertia.
It continues its expansion through the second and third rings of
nozzles, acting on the buckets of the wheel in the second and
third stages.   The type shown is a simple impulse type.
   In addition to this general classification, turbines are also
classed as to their number of stages, and as to whether they are
designed for "bleeding" steam at a pressure intermediate between
the supply and exhaust for use in process work, and as to whether
they operate condensing or non-condensing; in a way very similar
to the classification of reciprocating steam engines.   There is
also the so-called mixed-pressure turbine in which (in addition
to the boiler steam passing through it) excess low-pressure steam
is taken from the system into one of the lower stages.
   The question of selection of a reciprocating steam engine or a
turbine depends upon the following factors.

(a) Nature of the load.
(b) Size (125 H.P. or below — engine; above — turbine).
(c) Floor space — turbine 10 per cent to 40 per cent of that required by reciprocating engines.
(d) Maintenance.
(e) Oil in exhaust.

It is probable that the steam engine or turbine selected will be connected to an electrical generator and the question of selection of the electrical system becomes a serious matter. Shall the electricity selected be alternating or direct current, and what voltage and wiring system? Where the process is electro-chemical, the requirements of the process itself largely influence the selection of the electrical constants. In general the same specifications apply for the chemical plant as are used for ordinary industrial work, that is, alternating high voltage for transmission, 2300 volts for distribution outside of buildings, and 220 or 440 volts for motors, with 110 volts for lights. In general, voltages higher than 440 should not be used in close proximity to chemical process equipment unless extreme precautions be taken, yet the author has seen 2300 volt, 4400 volt, and even 13,200 volt equipment so used with perfect safety. In order to accomplish this, however, layout and operations were undertaken under unusual conditions. Where alternating current is used, and this is almost universal, three phase and sixty cycle are standard and preferred.

In the selection of the motor, the moot question of group vs. individual drive becomes important. Each problem must be studied separately; in general, group drive is preferred where the power requirements of the individual machines are small, the machines are grouped closely together, and fume or splash conditions require the placing of the motor a considerable distance from the chemical unit, as for example, in a separate house. Individual drives, although more costly, are more convenient and flexible, and become a real necessity when the horsepower per machine is large, say above 25 H.P.

*Other Types of Prime Movers.* — This chapter has emphasized the steam cycle for the obtaining of mechanical power, because of its great use in the chemical industry, but mention must be made of several other common types of prime movers.

Internal combustion engines operate on either gaseous or liquid fuels, and may be subdivided into 4-cycle (i.e., 4 strokes

per cycle) and 2-cycle. Other methods of classification are single or double-acting engines (one or both sides of piston used) and horizontal or vertical. Gas engines are always of the explosion type, oil engines may be either of that type (as is the case with the gasoline engine) or may operate on the slower burning Diesel cycle.

From the viewpoint of the efficiency of the conversion of fuel into *mechanical power*, the internal combustion engine is superior to the usual small or medium-sized steam engine with which it competes (25 per cent to 35 per cent as against 3 per cent to 12 per cent). This efficiency figure, however, is not the determining factor for selection, or true economy, which must take into consideration the cost of fuel and operating labor, the fixed charges on the investment and should further include a credit for the steam or hot water if used for further processing.

**Compressors.** — Eliminating the very special case of the ammonia compressor for refrigeration, compressors in a chemical plant are usually of two general classes:

First, low-pressure fans and blowers, for moving a relatively large volume of air at pressures rarely exceeding an ounce, and usually only a few inches of water. These are used for ventilation, for draft under boilers, for heat transfer in driers, etc.

Second, high pressure, measured in pounds per square inch, is obtainable by one of three classes of compressor:

(*a*) Rotary blower.
(*b*) Piston compressor.
(*c*) Turbo compressor.

These three types have each its own field, but because of improvements are so rapidly expanding this field that they are now becoming more competitive. Generally speaking, the rotary blower is preferred for pressures from ½ lb. to 3 lbs.; the piston compressor for all pressures higher; with the multi-stage turbo blower competing with both whenever the quantity of air is sufficient to permit it to operate efficiently. Where the quantity is small, the rotary may be used up to 10 lbs.; above that for small quantities the piston type; for large quantities the turbo will give satisfaction from 2 to 125 lbs. In both the piston and turbo-compressors several stages are used for the higher pressures, and the air is cooled between stages to absorb part of the heat

of compression. In this respect compressors are the converse of multi-stage steam engines and turbines, previously discussed. Air compressing may also be accomplished by means of steam jets, or hydraulically, but as both these types of installations are rare, they will not be further discussed here.
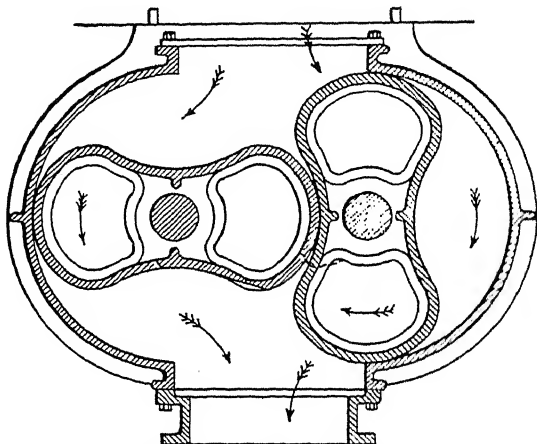


Fig. 16.   Rotary Blower.

The rotary blower (Fig. 16) consists of two displacers. The shafts rotating it are geared together so as to cause them to rotate, and at the same time maintain continuous contact with each other and with the inner surface of the casing. This picks up air on the suction side and transfers it to the discharge side, in so doing builds up the pressure.



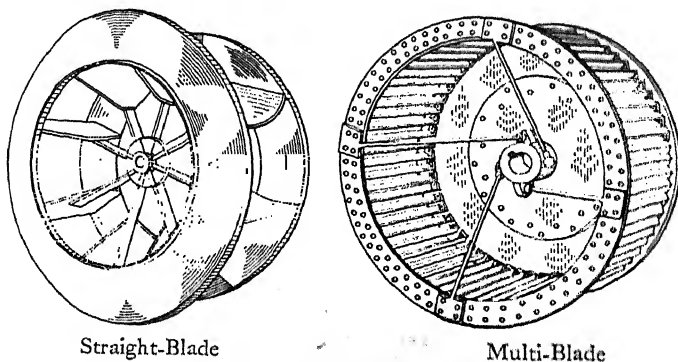Straight-Blade                    Multi-Blade
Fig. 17.   Centrifugal Fan Rotors.

There are numerous types of centrifugal fans, but the rotors of two principal types are shown in Fig. 17. With the straight blade, or radial blade fan, when operated at constant speed, the total pressure developed decreases as the output of the fan is increased. The multi-blade fan increases the total pressure as its output is increased.

The normal air pressures required in chemical plants are for:

(*a*) Agitation; 3 to 10 lbs.
(*b*) Press cake drying, etc.; 20 to 30 lbs.
(*c*) Acid lifts, sand blasting, air hoists, rock drills and tools, atomizing, etc.; 60 to 100 lbs. per square inch.

Pumps other than those used in the boiler plant are distinctly chemical equipment and are discussed elsewhere in this book.

**Refrigeration.** — Many chemical processes require a lower temperature than can be obtained from the atmosphere or the water available for cooling, and in such cases mechanical refrigeration must be employed. In recent years many new refrigeration methods have been introduced, but inasmuch as they have not yet come into general use, discussion is not herein included. Air, carbon dioxide, sulfur dioxide, ethyl chloride, methyl chloride, nitrous oxide, and various hydrocarbons are used in special applications as the refrigerating medium, but by far the most universally used refrigerant is ammonia, and our discussion will be limited to this.

Two general processes are available for ammonia refrigeration, the compression and the absorption. Owing to the splendid mechanical development of the compressor, it has become almost universal, but the chemical engineer will find many places where the absorption process should be used, and a careful study before deciding will pay well. The operation of the absorption system is more similar to that of a chemical plant, and the only moving part is a liquid pump; whereas the heart of the compression system is the gas compressor, an expensive and highly refined example of mechanical equipment.

The rating of both the absorption and compression systems varies with the required temperature; in general, the lower the temperature the greater the relative economy in both operation and investment cost of the absorption system. At ice making temperatures, however (brine 10°–16° F., ammonia 5° F., or 18 lbs., or higher), the compressor is less costly in investment.

All refrigerating equipment is rated in "tons of refrigeration," where the ton is defined as the heat absorbed by 2000 lbs. of pure ice melting to water at 32° F., assuming the latent heat of water to be 144 B.t.u. per lb.    This rating is further expressed as a function of time, all refrigerating calculations being made on a 24 hour basis.    A ton of refrigeration, therefore, equals 2000  lbs. $\times$ 144  B.t.u./lb. = 288,000  B.t.u.  per  24  hours = 12,000 B.t.u. per hour = 200 B.t.u. per minute.    (Note that the ice melting or refrigerating effect in tons is always less than the heat absorbed in ice making, so that the ice making capacity in tons of a refrigerating machine is from ½ to ⅔ its refrigerating capacity.    The extra heat absorbed is that required to cool the water to 32° F., to cool the ice from 32° F. to the mean temperature of all the ice in the brine tank, and to make up for radiation and other heat transmission losses in the system.)

After the refrigerating system has been selected, the engineer may then select one of three methods of utilizing it.    He may

(*a*) Make ice, transport the ice to the place of required heat abstraction and effect the required cooling either by direct contact (as immersion in the vessel containing the chemical) or by indirect contact (as through the jacket walls).

(*b*) Carry the compressed (liquified) refrigerant directly to the vessel to be cooled and therein expand it in suitable coils or jackets returning the expanded gas—direct expansion.

(*c*) Expand the refrigerant near the source of compression, utilizing it to cool brine, then pump the brine to and from the vessel to be cooled — indirect expansion.

Numerous factors enter into the selection of such a system, but after the questions of special hazard due to the chemicals and nature of the reaction have been eliminated, the usual factors entering will be found to prescribe ice where there is a large amount of heat to be abstracted very rapidly but which abstraction occurs only infrequently; where the load is isolated and relatively distant, direct expansion is cheaper; where there is a grouping of the load with fairly constant temperature requirements brine circulation will be preferred.

### PROBLEMS

1. Local Basic Costs: (*Note:* The text will not help you in answering Problem 1, but each engineer should know the answers as part of his daily work; these costs are

fundamental and vary with amounts used and localities. Approximate figures only should be borne in mind.)

Cost of coal per ton delivered; kinds normally used and heat values.

Cost of gas per 1000 cu. ft.; heat value and pressure supplied.

Range of cost of electricity, under following classes:

(a) Lights.

(b) Small power users, low voltage.

(c) Large power users, high voltage.

(d) Most favorable contracts for 24 hour use;--a use that can be made typical for chemical plants.

(e)

Cost of steam if sold by public utility.

Cost of water; by what unit is it sold?

Range of cost of fuel oil, and heat value.

Cost of ice: (a) Small users. (b) Large platform purchasers.

Is there any other source of heat peculiar to your locality and obtainable at a usable cost?

Cost of following basic chemicals, in carload lots:

(a) Sulfuric acid.

(b) Salt (Sodium chloride).

(c) Caustic soda (Sodium hydroxide).

(d) Soda ash.

(e) Nitric acid.

(f) Hydrochloric acid.

(g) Iron (any form).

(h) Copper (any form).

(i) Zinc (any form).

What are the starting rates per hour for following classes of labor:

(a) Unskilled labor.

(b) Pipe fitter.

(c) Machinist.

(d) Lead burner.

(e) Fireman.

(f) Licensed steam engineman (frequently erroneously called "stationary engineer").

2. After you have finished your plant layout for a new chemical process, you estimate that it will require a continuous and steady steam flow of 35,000 lbs. of steam per hour at a pressure of 100 lbs. per square inch. How many boilers would you install; what would each be rated at, and what pressure should they be set at?

3. Recording meters show the following conditions for one hour in your boiler plant burning soft coal: $CO_2$—10 per cent; flue gas temperature 650° F. What is the probable boiler efficiency?

# FLOW OF HEAT

J. C. OLSEN, Ph.D., D.Sc.

Many chemical engineering operations require that heat should flow from one body to another. Such operations as evaporation, distillation, condensation, and drying depend for their efficiency upon the transfer of heat. It is impossible to design the apparatus for these operations without understanding the conditions under which heat flows from one body to another.

**Methods of Heat Flow.** — Heat may flow by any one, combinations, or all, of three methods, namely: radiation, conduction, and convection. In each case the flow of heat is from the warmer to the cooler body. The physical state of the substances determines the method by which the heat flows. Transfer of heat by convection can take place only in fluids whether gases or liquids. Heat can be transmitted through solids only by conduction.

**Conduction.** — Transfer of heat by conduction is a molecular phenomena as it is believed that the temperature of a given body is a function of the kinetic energy of its molecules which in turn is a function of the velocity and weight of the molecules. Transfer of heat by conduction consists therefore in the transfer of some of this kinetic energy of the molecules of the hot body to the molecules of the colder body. The transfer by conduction takes place through impacts between the molecules. As these are much closer together in liquid and solid bodies, the transfer of heat is much more rapid than in gases, as the impacts of molecules are much more frequent. If fluids are in motion, the transfer of heat is more rapid because the molecular contacts become much more frequent.

## Heat Transfer by Radiation

The flow of heat by radiation is independent of the physical medium which is present between the hot and cold body provided

the medium is transparent.   Heat will flow by radiation through a gas at the same rate as through a vacuum.   This is not true if the gas contains suspended solid or liquid particles.

In most practical cases all three methods of flow of heat are met with.   In an evaporator, for instance, the heat may flow by radiation from the fire to the walls of the evaporator, then through these walls by conduction into the boiling liquid, through which it will be distributed by convection currents.   Even when the heat is supplied to the evaporator by means of steam, the steam must be produced by transfer of heat by radiation from the fire under the boiler through the boiler plates into the boiling water.

Only a small portion of the energy radiated from a hot body, as in a combustion process, is in the form of light.   The larger part of the energy is radiated in wave lengths much longer than light waves.   Of the heat waves the energy radiated by those of relatively short wave lengths is very much greater than from the waves of relatively greater wave length.   This is particularly true at high temperatures.   The total energy radiated is proportional to the fourth power of the temperature.

**Stefan-Boltzmann Law.** — The law governing the transfer of heat by radiation is known as the Stefan-Boltzmann law and may be expressed as follows: $Q = a(T^4 - T_0^4)$.   $T$ and $T_0$ are the absolute temperatures of the hot and cold bodies between which the heat is radiated.   " $a$ " is a factor dependent upon the nature of the hot body and to some extent upon its temperature.

**Black Body.** — The properties which cause a body to radiate energy also cause it to absorb energy.   In other words, the absorbing and radiating properties of a given body under the same conditions are identical.   The highest radiating and absorbing properties have been found to be associated with a dark color and a rough surface.   The ideal substance which would absorb 100 per cent of the radiant energy falling upon it is known as a " black body."   Such a body would reflect or transmit none of this energy.   No such body is known but substances are known which approach it in absorbing properties.   The factor " $a$ " for a black body has been determined to be $1.62 \times 10^{-9}$ B.t.u. per square foot per hour.

This amount of energy will be radiated only if the colder body is of such a size and so placed with reference to the hot radiating

body that it subtends a spherical angle of 180° for the surface of the hot body under consideration. Under these conditions all the radiant energy will be received by the colder body.

**The radiating power** of various solids relative to the ideal black body as the standard varies greatly. Polished metals may have values as low as 10 per cent, while rough and oxidized metals may have values as high as 90 per cent. If the radiating power of a given solid is known it is possible to calculate the amount of radiation in a given case from the area and the temperature. The most important factors in transferring heat by radiation are temperature, surface, and the relative position of the colder or receiving body. As radiation increases as the fourth power of the temperature, it is obvious that even a small increase of the temperature of the hot body greatly increases the amount of radiation.

### Heat Transfer Between Gases and Solids

When gases are in contact with solids, heat will flow from the warmer to the colder body. If the solid is the hotter, heat may pass partly by radiation to other solids and partly by conduction to the gas. The condition of the gas has a very important influence on the rate and mode of heat transfer. It is believed that in all cases a stationary film of gas is present on the surface of the solid. The thickness of this film depends upon the rate of flow of the gas and its temperature. This film becomes thinner as the velocity of the gas parallel to the solid surface increases.

**Gas Film.** — Heat from the solid is transmitted through this stationary gas film by conduction. As the thermal conductivity of all gases is very low, the heat transfer through the gas film is very slow. If the velocity of the gas stream is sufficient to produce turbulent flow, the transfer of heat from the stationary gas film·to the main body of the gas is rapid as the hot molecules are carried away mechanically by the gas stream. The molecular weight and specific heat of gases will also affect the rate of heat transfer.

**Shape Factor.** — There is some evidence to show that the " shape factor " of the gas stream influences the rate of heat transfer. The shape factor is defined as the ratio of the cross sectional area of the gas stream to the perimeter of the heating

surface. For instance, if the gas is passing through a heated pipe the area of the gas stream will be the cross sectional area of the pipe which will be equal to $\pi r^2$. The corresponding perimeter of the heating surface will be $2\pi r$. Therefore the shape factor will be $\pi r^2/2\pi r$ or $\frac{1}{2}r$. It is reasonable to suppose that as the shape factor increases the heat transfer will decrease.

As the thermal conductivity of gases increases with temperature, it is reasonable to suppose that the heat transfer from solids to gases would increase with temperature.

**Over All Conductance.** — The amount of heat which passes through the gas film on a solid body is given in B.t.u. per square foot per °F. per second or other convenient unit of time. In a given case such as the heating of air or other gas by means of steam pipes the over all conductance will result from the conductance of the liquid film on the steam side, the conductivity of the metallic pipe, and its thickness, and the conductance of the gas film. If $K_1$ and $K_2$ represent the conductance of the water and gas films, $X$ the conductivity of the wall of the steam pipe, and $d$ its thickness, then

$$\frac{1}{U} = \frac{1}{K_1} + \frac{d}{X} + \frac{1}{K_2}$$

and

$$U = \frac{1}{\dfrac{1}{K_1} + \dfrac{d}{X} + \dfrac{1}{K_2}}$$

where $U$ equals the over all conductance. A study of these resistances to the flow of heat will show that the conductivity of the metal wall as well as the liquid film on the steam side is so high compared to that of the gas film that the rate of flow of heat will be determined by the resistance of the gas film. The transfer of heat from steam through a metal wall to boiling water will generally be from 300 to 500 B.t.u. per square foot per hour per °F., while if the boiling water is replaced by a gas the heat transfer will be only about 1/100 of this amount.

**Velocity of Gas.** — The conditions controlling heat transfer through the gas film are of primary importance. The most important of these are the density and velocity of the gas stream

and the heating area. These may be expressed in terms of pounds of gas per square foot per second.

It has been experimentally demonstrated that the coefficient of heat transfer, that is the number of B.t.u. passing from or to the metal from air or other gas per square foot per degree F. per second is a function of the velocity of the gas in terms of pounds of gas per square foot per second.

The published results differ considerably. According to a study made by Professor W. L. Badger [1] the most reliable results range from a heat transfer of 0.77 at a gas velocity of 0.1 pound of gas per square foot per second, to 33 at a gas velocity of 15. The equation of the curve developed by Badger is $K = 4.32 \ (w/a)^{0.75}$, in which $K$ is the heat transfer, $w/a$ is the gas velocity in the units given, $w$ being the total weight of gas passing per second and $a$ the area of the path in square feet. The values are given for air flowing inside of tubes of from one-half to two inch diameter at temperatures not over 400° F. For gases other than air the coefficients to be used are $CO_2$ 3.58, coal gas 11.6 and superheated steam 8.06.

**Superheated Steam.** — It is to be noted that the coefficient of heat transfer for superheated steam is of the order of magnitude of permanent gases and not that of saturated steam which is approximately 100 times as large. As a heating agent, super-heated steam is very inefficient, requiring a very large surface for heat transfer as compared with saturated steam. It has the further disadvantage as a heating agent that, as it gives up heat, its temperature falls rapidly until it reaches the condition of saturated steam. The coefficient of heat transfer for superheated steam is of value to the chemical engineer in the design of equipment for the production of superheated steam from saturated steam when it is required for steam distillation, as in the glycerine industry.

### HEAT FLOW BY CONDUCTION

The flow of heat through a homogeneous body by conduction is proportional to (a) the thermal conductivity of the material, (b) the difference in temperature between the two points considered, (c) the area through which the heat flows, (d) inversely proportional to the distance between the two points.

[1] Heat Transfer and Evaporation, p. 49.

**Laws of Heat Flow.** — The flow of heat follows the same laws as the flow of electricity. The difference in temperature between the hot and cold body corresponds to the difference in potential measured in volts. This difference in voltage gives a measure of the electromotive force which produces the flow of electricity just as the temperature difference produces the flow of heat. The resistance to the flow of electricity is measured in ohms which are a function of the length and cross sectional area and the material of which the conductor is made. The resistance to the flow of heat is the reciprocal of the conductivity of the material for heat.

In the case of flow of heat all of the necessary values may be easily measured with the exception of the thermal conductivity which must be obtained by careful experimentation upon the material in question. The unit used in engineering work in the English system for thermal conductivity is the number of B.t.u. flowing per square foot of area, per foot of thickness, per degree F. temperature difference per hour.

Using the following symbols:

$Q$ = heat transferred in B.t.u. per hour.

$x$ = thermal conductivity.

$A$ = area of path in square feet.

$L$ = length of path in feet.

$t_1$ = higher temperature °F.

$t_2$ = lower temperature °F.

the total heat transferred is expressed by the following formula:

$$Q = \frac{xA(t_1 - t_2)}{L}.$$

The conductivities of a number of common substances are given in the following tables.

It will be noted that the metals in general, including electrode carbon, have a conductivity at least a hundred times that of the non-metals and the liquids, while the gases have a much lower conductivity still. These great differences have an important bearing on heat flow in chemical engineering equipment.

ThERMAL CONDUCTIVITIES IN B.T.U., PER FOOT, PER SQ. FT., PER °F. PER HR.

### (a) Metals

| Material | Experimental Temperature Range °F. | Conductivity |
|---|---|---|
| Aluminum | 32–212 | 85 |
| Brass, yellow | 32–212 | 55 |
| Copper, pure | at 68 | 238 |
| | at 212 | 220 |
| Iron: | | |
| Pure | at 76 | 37 |
| Wrought | 35–527 | 40 |
| Cast, 3.5 per cent C. | at 86 | 36 |
| Lead | at 59 | 20 |
| Nickel | 68–392 | 32 |
| Platinum | 64–212 | 41 |
| Silver | at 64 | 243 |
| Steel | at 82 | 25 |
| Tin | at 32 | 35 |
| Zinc | at 64 | 64 |

### (b) Non-Metals

| Material | Experimental Temperature Range °F. | Conductivity |
|---|---|---|
| Asbestos | 100–1000 | 0.12 |
| Brick: | | |
| Carborundum | at 1800 | 5.6 |
| Building | at 1800 | 0.8 |
| Kieselguhr | at 1800 | 0.4 |
| Sil-O-Cel | at 1800 | 0.03 |
| Brick and mortar wall | ........ | 0.4 |
| Portland cement, neat | at 95 | 0.5 |
| Cork | 122– 392 | 0.03 |
| Electrode carbon | 212–1700 | 32 |
| Glass, flint | 50– 59 | 0.3 |
| Infusorial earth (12.5 lbs. per cu. ft.) | at 122 | 0.05 |
| Magnesia | 68– 310 | 0.04 |
| Rubber | at 220 | 0.1 |

### (c) Gases

| | At 32° F. | At 212° F. |
|---|---|---|
| Air | 0.0137 | 0.0174 |
| Carbon monoxide | 0.0131 | ..... |
| Carbon dioxide | 0.00804 | 0.0120 |
| Oxygen | 0.0138 | 0.0180 |
| Nitrogen | 0.0138 | 0.0174 |
| Hydrogen | 0.092 | 0.123 |
| Methane | 0.0174 | ..... |
| Steam | 0.0095 | 0.0129 |

(d) *Liquids*

|  | At 86° F. | At 167° F. |
|---|---|---|
| Normal pentane | 0.078 | 0.074 |
| Kerosene | 0.086 | 0.081 |
| Petroleum ether | 0.075 | 0.073 |
| Menthanol | 0.122 | 0.119 |
| Ethanol | 0.104 | 0.100 |
| Ispropanol | 0.089 | 0.088 |
| Normal butanol | 0.097 | 0.094 |
| Iso-amyl alcohol | 0.086 | 0.084 |
| Ethyl-ether | 0.079 | 0.075 |
| Acetone | 0.103 | 0.097 |
| Carbon bisulfide | 0.092 | 0.087 |
| Water | 0.347 | 0.372 |

When attempting to use these values to calculate the flow of heat in such equipment it must be remembered that the heat does not flow through a single homogeneous body such as steel. It generally must flow through several different substances. For instance, it may flow from steam into steel and then into the liquid being heated. When flowing through fluids, such as steam or liquids, it may pass by conduction or by convection.

**Viscous and Turbulent Flow.** — It has been found that liquids flow in two entirely different methods known as viscous and turbulent flow. In viscous flow the liquid moves in layers parallel to the tube wall and for this reason it is often spoken of as stream line flow. Heat can pass through such a liquid only by conduction. In turbulent flow the particles of the liquid move in all possible directions. Under these conditions the heat transfer is by convection and is very rapid. At low velocities the motion is stream line but as the velocity is increased it changes to turbulent flow. The velocity at which this change takes place is known as the critical velocity. It is constant for a given liquid and temperature.

**Reynold's Criterion.** — The character of the flow of fluids has been shown to be dependent upon the density as well as the viscosity of the liquid in addition to its velocity. Since the viscosity varies with the temperature for a given liquid, this is also a factor. When flowing through pipes, the diameter of the pipe is also significant. The relation among these factors have been

expressed by Reynold's Criterion $DVp/Z$ in which

$D$ = inside diameter of pipe in inches.
$V$ = average velocity of fluid in feet per sec.
$p$ = density of fluid in pounds per cubic foot.
$Z$ = viscosity of fluid in centiposes. (This value is equal to viscosity relative to water at 70° F.)

When $DVp/Z$ = 7.5 to 9.5 the critical velocity is reached. The value 7.5 holds for iron pipe while 9.5 holds for brass or copper pipe. The essential difference seems to be the roughness or smoothness of the pipe, rough pipe giving the lower values and smooth pipe the higher values.

The critical velocity of a number of fluids is given in the following table:

CRITICAL VELOCITY OF FLUIDS * IN TWO INCH PIPE

|  | °F. | Absolute Pressure Atmosphere | Specific Gravity | Relative Viscosity | Critical Velocity ft./sec. |
|---|---|---|---|---|---|
| Hydrogen. | 70 | 1 | 0.0000834 | 0.0088 | 6.2 |
| Air...... | 70 | 1 | 0.0012 | 0.0184 | 0.904 |
| Air...... | 70 | 10 | 0.0012 | 0.0184 | 0.0904 |
| Steam.... | 212 | 1 | 0.00060 | 0.0120 | 1.18 |
| Steam.... | 357 | 10 | 0.00524 | 0.0144 | 0.162 |
| Water.... | 68 | any | 1.0 | 1.0 | 0.059 |
| Refined oil | 68 | any | 0.90 | 10.0 | 0.65 |
| Crude oil.. |  | any | 0.963 | 3450 | 211 |

* Principles of Chemical Engineering, Walker, Lewis and McAdams, p. 77.

These critical velocities are so low that in practice the velocities employed are invariably above the critical values with the possible exception of very viscous liquids such as crude oil.

**Liquid Films.** — It has also been found that the velocity of a liquid is very much reduced near the confining wall, resulting in an almost stagnant layer or film of liquid near the wall. This layer of liquid moves in viscous flow. The thickness of this film will depend upon the velocity of the flow of the liquid, its temperature and the viscosity of the liquid. As the viscosity decreases with increase in temperature, the thickness of the film

decreases with temperature as well as with velocity, while the transfer of heat increases.

**Gas Films.** — The transfer of heat from steam or other saturated vapors to colder solid surfaces is very rapid on account of the high energy content of the molecules in the vapor state, which is liberated on condensation to the liquid state. Steam and other vapors generally contain non-condensable gases such as $CO_2$, $O_2$, $N_2$, etc. In the case of steam these gases are derived from the water used in the boiler. These gases are collectively known as air. When the molecules of water vapor condense, these gases remain on the surface and form a film of gas through which heat passes very slowly. A film of water through which the heat must pass is also formed on the condensing surface.

**Total Heat Transfer.** — The transfer of heat from steam to a liquid being heated therefore involves the passage of the heat through the following layers: (*a*) film of air, (*b*) film of water, (*c*) metallic wall, (*d*) film of liquid, (*e*) main body of liquid. Almost invariably the metallic surface will be coated with a deposit of scale from the liquid or oxide of the metal. This would furnish two more layers through which the heat must pass.

The resistance of each of these films is a function of the conductivity of the specific material and its thickness. As the flow of heat is also proportional to the temperature difference between the hot and cold liquid, mathematically the amount of heat flowing may be expressed by the following formula:

$Q$ = total heat passing through unit surface in unit time.

$t^1 - t^2$ = temperature difference.

$r^1, r^2, r^3$, etc. = resistance to flow of heat.

$$Q = \frac{t^1 - t^2}{r^1 + r^2 + r^3, \text{ etc.}}.$$

The resistance to the flow of heat of a given material is equal to the reciprocal of its conductivity so that representing conductivities by $l^1, l^2, l^3$, etc., the expression becomes

$$Q \quad \frac{t^1 - t^2}{\frac{1}{l^1} + \frac{1}{l^2} + \frac{1}{l^3}, \text{ etc.}}$$

The conductivity and thickness of the solid films may be readily determined. Very little is known of the thickness of the gas and liquid films, although an approximation may sometimes be made. Wherever the thickness and conductivity of the films is known or can be determined, it is possible to calculate the resistance to the flow of heat. It has been possible in some cases to determine by a process of elimination the film coefficient which can be used in the calculation of the overall coefficient of transfer of heat.

Calculation of the flow of heat through metal surfaces neglecting the gas and liquid films may be readily made.

*Example.* — Calculate the heat flow through a lead pipe ¾ inch inside diameter having walls ⅛ inch thick and ten feet long, the temperatures of the inside and outside surfaces being 212° F. and 62° F.

*Solution.* — The average diameter of the pipe will be

$$\frac{\frac{3}{4} + 1}{2} = 0.875 \text{ inch.}$$

The average area will be

$$\frac{0.875 \times \pi \times 10}{12} = 2.29 \text{ sq.ft.}$$

The specific conductivity for heat of lead is 20. The total heat flow will therefore be

$$Q = \frac{20 \times 2.29 \times (212 - 62)}{0.125/12} = 660,600 \text{ B.t.u. per hr.}$$

The heat flow per hour per sq.ft. per °F. will be

$$\frac{660,600}{2.29 \times 150} = 1923 \text{ B.t.u.}$$

This value is very much higher than that realized in practice, the reason being that no account has been taken of the resistance of the surface films on the pipe.

**Surface Films.** — If in this case the heating agent is steam, a film of condensed water will be present on the inside of the pipe. There will also be a stationary film of water on the outside of the pipe in contact with the cold water. If each of these films be

assumed to be 0.01 inch thick it becomes possible to calculate the heat flow with this added resistance.

The formula for calculating this heat flow will be

$$Q = A \frac{t_1 - t_2}{\frac{l_1}{\lambda_1} + \frac{l_2}{\lambda_2} + \frac{l_3}{\lambda_3}, \text{ etc.}}$$

If unit area and unit temperature difference be taken the formula becomes

$$Q = \frac{1}{\frac{l_1}{\lambda_1} + \frac{l_2}{\lambda_2} + \frac{l_3}{\lambda_3}, \text{ etc.}}$$

$l_1$, $l_2$, $l_3$, etc. being the thickness of the films in feet, we have for the combined water films

$$\frac{.02}{12} = .00167 \text{ ft.}$$

and for the lead

$$\frac{0.125}{12} = .0104.$$

The specific conductivity of water being 0.417, the heat flow will be

$$Q = \frac{1}{\frac{.00167}{0.417} + \frac{.0104}{20}} = 222 \text{ B.t.u. per hr.}$$

This value for the coefficient of heat transfer from steam to water through a clean lead pipe is very close to that obtained in practice.

**Copper Pipe.** — If, in the above calculation, the conductivity for copper (220) be substituted for that of lead, a value will be found for the conductivity of copper pipe of the same dimensions. The result will be found to be 247. This result is only slightly higher than the result found for lead, although the conductivity of the copper is eleven times that of lead. This arises from the fact that the film resistance is the same in both cases and is very much greater than the resistance of the metals.

**McAdams Formula.** — All conditions which affect the surface films will be found to affect the transfer of heat. The most important of these are the viscosity and velocity of the liquid, the diameter and the length of the pipe. W. H. McAdams has developed a formula which gives the film conductivity ($L$) expressed in B.t.u. per sq.ft. per °F. per hr. for transfer of heat from non-boiling liquids.

$$h = \frac{5.06}{D^{0.2}} \left( \frac{V}{Z_b} \right)^{0.8} \left( 1 + \frac{50}{r} \right) R.$$

In this equation

$h$ = the conductivity of the film.

$D$ = inside diameter of the pipe in inches.

$V$ = average mass velocity of the liquid flowing through the pipe expressed as pounds per sq.ft. of cross section of the pipe per second.

$Z_b$ = viscosity of the liquid film relative to water at 68° F.

$r$ = ratio of the length of the pipe to its inside diameter.

$R$ = thermal conductivity of the liquid relative to that of water (water = 0.329).

All of these values are readily obtained with the exception of $Z_b$. This is the viscosity of the liquid film. This is a function of the temperature. In this case the temperature of the film must be obtained and not the average temperature of the liquid in the pipe. This temperature will be an average between the temperature of the tube wall and the liquid.

**Mean Temperature Difference.** — When the over all coefficient of heat transfer has been obtained, the total heat transfer in a given piece of apparatus is equal to the product of this value and the temperature difference, time and total surface. When the temperature difference is not the same in all parts of the apparatus, the mean temperature difference must be found. If the temperature differences in various parts of the apparatus do not differ widely, the average of several observations may be safely taken as the mean value.

When the temperatures vary widely as when a hot liquid flowing through a pipe is being cooled, the calculation is less simple. In Fig. 18 the temperature differences are represented by $t_1 - t_3$ and $t_2 - t_4$.

The mean temperature difference is found by the following formula:

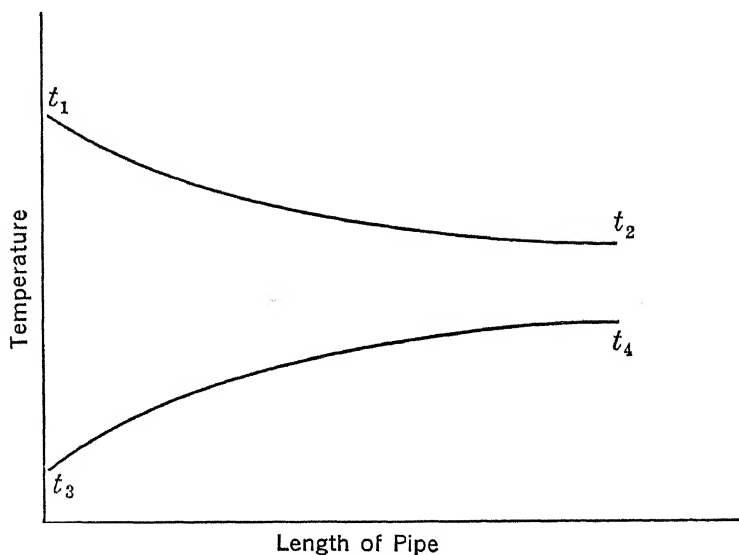$$t = \frac{(t_1 - t_3) - (t_2 - t_4)}{2.3 \log (t_1 - t_3)}$$



Fig. 18.

In many chemical engineering operations it is necessary to heat one liquid and cool another. Both of these operations can be advantageously carried out in a single apparatus in which the hot liquid is used to raise the temperature of the cold liquid. This involves the transfer of heat from liquid to liquid.

**Double-Pipe Heat Interchanger.** — In the transfer of heat from liquid to liquid, the apparatus used is called a heat interchanger. The form of apparatus sometimes used for this purpose consists of two pipes of unequal diameters mounted concentrically leaving a uniform annular space between the smaller inside and larger outside pipe. When the hot and cold liquids are pumped through the smaller pipe and the annular space respectively, interchange of heat takes place rapidly. It has long been known that the rate of heat transfer increases with increase in the velocity of either liquid. Hausbrand gives the

following formula using metric units for heat transfer between two liquids moving at different velocities in copper tubes:

$$K = \frac{200}{\dfrac{1}{1 + 6\sqrt{V_1}} + \dfrac{1}{1 + 6\sqrt{V_2}}}$$

$K$ = the coefficient of heat transfer.

$V_1$ and $V_2$ = the velocities of the hot and cold liquids.

This formula would indicate that the effect on the heat transfer of changing the velocity of either the hot or the cold liquid is the same and that the change is proportional to the square root of the velocity.

Richter [2] has published results which differ somewhat from these results. He used a double pipe apparatus and found that the rate of heat transfer varied with the form of the apparatus as well as with the relative pipe diameters. He found that the greatest heat transfer took place in the apparatus which was in the form of a helix. For the straight pipe he developed the following formula using the English units:

$$K = \frac{62.7}{\dfrac{1}{1 + 5V_h{}^{.57}} + \dfrac{1}{1 + 5V_c{}^{.57}}}$$

$K$ = heat transfer in B.t.u. per sq.ft. per hr. per °F.

$h$ = velocity of the hot liquid in ft. per sec.

$c$ = velocity of the cold liquid in ft. per sec.

For the heat interchanger in the form of a helix he developed the following formula:

$$K = \frac{76.2}{\dfrac{1}{1 + 5V_h{}^{.60}} + 1 + 10V_c{}^{.50}}$$

A study of apparatus having different pipe diameters showed that these dimensions had a marked influence on the rate of heat flow. $x$ and $y$ were used to designate the dimensions shown in the diagram.

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[2] Geo. A. Richter, Double-Pipe Heat Exchanges, Trans. A. I. Ch. E., vol. xii, pt. 2, p. 147.

The ratio $x/y$ was computed for the apparatus used and was found to be equal to 0.687, 0.48 and 0.406. The lowest heat transfer was given by the apparatus having the ratio 0.687 and the highest heat transfer by the apparatus with the ratio 0.406.
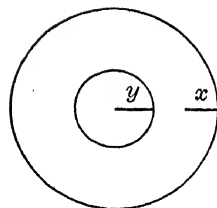
**Multi-Tubular Heaters.** — Only a limited amount of liquid can be satisfactorily heated in the double pipe heat interchangers. Where larger capacity is required, the so-called multi-tubular heat exchangers must be employed. This apparatus consists of a number of parallel tubes the ends of which are expanded into tube sheets, the whole being surrounded by a cylindrical casing which is provided with distribution heads at each end. The heating steam or vapor is introduced into the space surrounding the tubes while the fluid to be heated is pumped into one distribution head through the tubes to the second distribution head from which it is discharged. See Fig. 28.

Apparatus of this type may be constructed with very large heating surface. This may result in a low velocity of fluid and therefore a low coefficient of heat transfer. This difficulty may be remedied by using a multi-pass heater. In this modification of the heater, baffles are placed in the distribution head so that the fluid flows through one section of the heating tubes and must return by another similar section. In this manner the length of pass of the fluid to be heated may be very much increased. This will correspondingly increase the velocity of the fluid flow and therefore the rate of heat transfer.

Apparatus of this type may be used for heat transfer from liquid to liquid or from liquid to gas or vice versa. A special case is transfer of heat from steam to a liquid. If the liquid is boiling the operation is called evaporation and will be considered in chapter III.

## CONDENSERS

Heat transfer apparatus designed to convert vapors into liquids is known as a condenser. The cooling agent is generally water which enters the apparatus cold and emerges hot. It is not usually heated to the boiling point, so that the heat transfer is from vapors to a non-boiling liquid.

Condensers are divided into two classes known as surface condensers and jet condensers. The surface condenser is an apparatus so constructed that the vapor is separated from the cooling water by the surface of pipes or similar apparatus. The heat must flow from the vapor being condensed through the metallic surface to the cooling water. The condensate is also kept separated from the cooling water. In the jet condenser on the other hand the vapor to be condensed is in direct contact with the vapor to be condensed and the condensate.

**Surface Condensers.** — In addition to condensing the vapor, surface condensers also usually serve to lower the temperature of the condensed liquid and therefore also act as coolers. In this part of the apparatus the flow of heat is from liquid to liquid, while in the condenser proper it is from vapor to liquid.

This type of condenser is used where it is desirable to collect the distillate without admixture with water. In such operations as the distillation of alcohol, petroleum and other hydrocarbons, essential oils, etc., surface condensers are invariably employed.

**Types of Surface Condensers.** — Three general types of construction are used for surface condensers, namely: helix, multiple pipe, and double pipe condensers or heat interchangers. The helix condenser consists of a single length of pipe coiled into the shape of a helix and enclosed in a suitable cylindrical container for the cooling water. The multiple pipe condenser consists of a basket of short lengths of pipe enclosed in a suitable container with inlet and outlet for the cooling water and for the vapor and condensate.

The double-pipe heat interchanger consists of a smaller pipe inserted in a larger pipe so as to leave an annular space for the passage of liquid or vapor. When used as a condenser the vapor would be passed through the inner pipe and the cooling water through the annular space within the outer pipe.

*Capacity.* — In accordance with the principles of heat transfer already given, the capacity of any one of these types of apparatus would be in proportion to the amount of surface, mean temperature difference, and coefficient of heat transmission. A considerable number of factors influence this coefficient as follows:

Vapors of all liquids have the same coefficient of heat transfer other factors being the same. As the heat of vaporization differs

for various liquids the amount condensed for a given amount of heat transmitted will be different.

There will be very little difference in the transmission of heat whether the vapors pass through the pipes and the cooling water outside or vice versa.

*Permanent Gases.* — Most vapors contain air or non-condensable gases which tend to accumulate in the pipes as the condensable vapor is converted to liquid. Such permanent gases reduce very materially the efficiency of the condenser and if allowed to accumulate would almost wholly prevent condensation. When condensers are operated in connection with vacuum apparatus the air pump continually removes such non-condensable gases. When condensing steam at atmospheric or higher pressures suitable exits must be provided for the non-condensable gases.

*Liquid Film.* — A layer of the condensed liquid is formed on the cooling tubes so that the heat must be transferred not only through the walls of the pipes but also through this layer of liquid. The character of this liquid and the thickness of the layer will have an important influence on the efficiency of the condenser. A heavy viscous liquid will interfere a great deal more than a light thin liquid. The condenser should be so constructed that this liquid will drain as completely as possible. When it is desired to cool this liquid before discharge from the condenser it must be so constructed and operated that the liquid will remain a sufficient time to give up its heat to the cooling water. Under these conditions a part of the apparatus will act as a cooler and the remainder as a condenser and therefore its capacity as a condenser will be proportionally reduced.

The mean temperature difference must be found by the formula already given for the coefficient of transmission of heat. The method of operation with reference to parallel or opposite flow of hot and cold liquids will also be of importance. In most permanent installations the opposite current flow is utilized in order to economize on the use of the cooling water.

The warmer the cooling water the more readily it will take up heat on account of the lower viscosity and the formation of convection currents but the lower will be the temperature difference. Oily substances coming over with the steam will diminish the conduction of heat of the condenser, owing to the formation of an oily film.

The velocity of the current of both steam and cooling water has a decided influence upon the amount of transfer of heat. In general, the transmission of heat increases with increase of velocity of either the steam or the cooling water. Various formulas have been derived from experimental data for calculating the effect on the coefficient of transmission of heat of changes in velocity of steam and cooling water. As it is difficult to duplicate conditions exactly, these formulas are applicable only in a general way.

**Jet Condenser.** — *The jet condenser* is an apparatus in which the cooling water comes into direct contact with the vapor to be condensed. (Fig. 27.) The condensate is mixed with or dissolved in the cooling water. This type of condenser is employed when the condensate is of no value and can be discharged to the sewer with the cooling water. In a great many operations when solutions are evaporated for the recovery of dissolved substances and the solvent is water, this type of evaporator is employed. It is cheaper to construct and operate than surface condensers and has the advantage of direct contact between the vapor and cooling water. This is desirable because the vapor is condensed by direct contact with the water at its surface from which it follows that the greater the surface of water exposed to the steam the more rapidly will the steam be condensed. Water may be distributed in a condenser in the form of (*a*) sheets, (*b*) jets or (*c*) drops. The ratio of surface to volume determines the condensing efficiency of a given volume of water.

If $S$ = surface and $V$ = volume, then $S/V$ will represent the condensing efficiency of a given portion of water. The following table gives this ratio for various forms of water distribution:

| Diameter | 2 | 4 | 6 | 8 |
|---|---|---|---|---|
| Sheet flowing, $S/V$.... | 0.5 | 0.25 | 0.1667 | 0.125 |
| Sheet falling, $S/V$..... | 1.0 | 0.5 | 0.333 | 0.25 |
| Jet, $S/V$............. | 2.0 | 1.0 | 0.666 | 0.5 |
| Drop, $S/V$.......... | 3.0 | 1.5 | 1.0 | 0.75 |

These ratios are readily calculated from the geometrical relation of volume to surface of the configuration given. For instance,

the volume of a sphere is given by the formula,

$$\text{vol.} = \frac{1}{3}\pi r^3$$

The surface $S = 4\pi r^2$

$$\frac{S}{V} = \frac{3}{r}$$

The ratio of the surface to the volume of two spheres varies inversely as their radii.

It is obvious from the table that drops are the most advantageous forms for the distribution of the water and that the drops should be as small as possible. There are difficulties in constructing and operating condensers entirely in the form of drops. For various reasons the other forms of distribution must also be used. Condensation of the steam takes place at the surface of the water which constitutes the boundary between the steam and the water. Condensation tends to cease as the temperature of the surface of the water rises. Transfer of heat from the surface to the interior of the water is slow on account of the low conductivity of water for heat, $x = 0.155$, that is, 0.155 gram calories pass in 1 sec. through a layer of water 1 sq. meter surface, 1 mm. thick, 1° C. difference in temperature.[3] The amount of heat that passes through a layer of water is directly proportional to the surface, time and difference in temperature and inversely proportional to the square of the thickness.

As the steam rapidly heats the outer layers of water but penetrates very slowly to the interior layers, the surface of the water must be great or the surface must be changed rapidly or the time of contact must be lengthened.

The time of contact may be increased by increasing the height of fall of the drops. The following table gives the increase in temperature resulting from increased height of fall, temperature difference being 1° C.

| Size of drops | 2 mm. | 2 mm. | 2 mm. | 3 mm. | 3 mm. |
|---|---|---|---|---|---|
| Time in sec. | 0.1 | 0.2 | 0.4 | 0.8 | 1.2 |
| Height of fall in mm. | 49.05 | 196.2 | 785 | 3139 | 6953 |
| Mean increase in temperature. | 0.204 | 0.270 | 0.351 | 0.338 | 0.384 |

[3] The conductivity of water in English units is given on page 43.

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| Mean increase in temperature | 0.204 | 0.270 | 0.351 | 0.338 | 0.384 |

[3] The conductivity of water in English units is given on page 43.

It will be noted that a very great increase in height of fall and time is necessary in order to secure any considerable increase in the mean temperature. It has been found that greater efficiency is secured by introducing shelves or catch plates to break the fall of the water or otherwise cause rapid mixing of the water in order to bring the colder water to the surface into contact with the steam to be condensed.

Jet condensers may be used to condense vapors at atmospheric or higher pressures or at lower than atmospheric pressures. When used with vacuum apparatus an air pump must be used to draw off the non-condensable gases. Provision must also be made for removal of the condensing water. This is generally done by providing an exit pipe of such length that the column of water is equal to the atmospheric pressure less the pressure of the vapors in the evaporator. Such a condenser is known as a barometric condenser.

When a condenser is operated in connection with vacuum apparatus, it performs an important function in maintaining the vacuum. For economy in installation and operation the capacity of the vacuum pump is limited to that necessary to remove only the non-condensable gases. It is the function of the condenser to remove the condensable vapors as rapidly as formed. If the condenser fails to do this, the pressure in the evaporator rises. The lowest pressure attainable in the evaporator is fixed by the temperature of the cooling water. For instance, since the vapor pressure of water at 102° F. is 2 inches of mercury, it would be impossible to maintain a pressure of less than this in the evaporator using cooling water of 102° temperature in the condenser.

The highest temperature to which the water in the condenser can be heated is the temperature of the vapor being condensed. This fixes a limit to the water efficiency of the condenser. As the vapor temperature in vacuum apparatus is low the quantity of cooling water used will be large.

It is desirable that the temperature of the non-condensable gases leaving the condenser through the vacuum pump be as low as possible as this reduces the volume to be removed by the pump and therefore reduces the power used for this purpose and permits the installation of a smaller pump. The non-condensable gases will always be saturated with water vapor when leaving the condenser. The higher the temperature of these gases the

greater will be the proportion of water vapor and the greater the absolute volume of the gas to be removed by the pump. This may be illustrated as follows:

Assuming a case in which the absolute pressure in the evaporator is 4 inches of mercury and the temperature 102° F., the vapor pressure will be 2 inches. In this case 50 per cent of the gases removed will be water vapor. If the temperature is reduced to 90° F. the corresponding vapor pressure will be 1.4 inches of mercury. The partial pressure of the air will be 2.6 and the percentage of air will be 65. This corresponds to a reduction of 23 per cent of the volume of the gases to be removed by the pump.

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W. L. BADGER. Heat Transfer and Evaporation, Chemical Catalogue Company.

E. HAUSBRAND. Evaporating Condensing and Cooling Apparatus, D. Van Nostrand Company.

### PROBLEMS

4. (*a*) Calculate the cooling surface required to cool in 5 hours 1000 gallons of aqueous solution from 212° F. to 80° F. by means of water at 60° F. leaving the opposite current flow apparatus at 185° F., $K$ being taken as 600 B.t.u. per sq. ft. per hour.

(*b*) Calculate the number of gallons of cooling water required.

(*c*) Calculate the number of feet of pipe of 1½ inch diameter required.

5. A pipe 1¼ in. diameter by 20 ft. long is surrounded by a second pipe 2 in. in diameter. 850 gallons of water per hour enter the inner tube at a temperature of 220° F. and leave at a temperature of 120° F. Another liquid flows in the opposite direction through the annulus entering at 60° F. and leaving at 190° F. Calculate the coefficient of heat transfer through the pipe wall.

6. A liquid, sp. heat .5, sp. gr. .8, is to be heated from 60° F. to 212° F.; at the rate of 3000 pounds per hour. It is passed through a copper coil heated by steam at 10 lbs. gage pressure. (*a*) How much steam will be required per hour? (*b*) What must be the length and diameter of the copper coil? (*c*) If a lead pipe were used what would be its length and diameter?

7. Calculate (*a*) the number of gallons of water, (*b*) the number of feet of 1 inch pipe required for the condensation of 200 pounds of steam per hour at 20 pounds pressure to water at 80° F. Assume $K$ to be 800 B.t.u., the cooling water to have an initial temperature of 50° F., and a final temperature of 180° F. in a counter current flow apparatus. (*c*) anb (*d*) Make the same calculations for a parallel flow apparatus, the final temperature of the cooling water being 120° F.

8. Design a plant for the evaporation of 50,000 gallons of 5 per cent NaOH to 40 per cent solution per day of 24 hours. Steam at 30 lbs. gage pressure is available and cooling water at 60° F. It is desirable to use the minimum amount of steam. Use the following data:

VAPOR PRESSURE AND BOILING POINTS OF NaOH SOLUTIONS

| Concentration gms., NaOH per 100 gms. of Solution | Vapor Pressure in mm. Hg. | | Boiling Points at 760 mm. °C. |
|---|---|---|---|
| | At 0°C. | At 100° C. | |
| 5................ | 4.4 | 729 | 101.2 |
| 10................ | 4.14 | 689 | 103 |
| 20................ | 3.25 | 578 | 108 |
| 30................ | 1.9 | 424 | 116 |
| 40................ | — | 230 | 128.5 |
| 50................ | — | — | 142 |

Calculate the heating surfaces required, also the cooling surface in the condensers employed. Give the pounds of water evaporated per pound of steam. Make a sketch of the plant and apparatus employed.

9. Air saturated with benezene vapor at 55° C. enters a tubular condenser having 150 × 2 in. internal diameter tubes at the rate of 7000 cu. ft. per minute. The air leaves the condenser at 25° C. Calculate the quantity of benzene condensed per hour by the condenser and the cooling surface required assuming that the water enters at 15° C. and leaves at 30° C. Calculate also the amount of benzene per hour which passes uncondensed from the apparatus. The film coefficient of condensing benzene may be taken as 340.

# CHAPTER III

## EVAPORATION

### A. L. WEBRE, M.E.

#### INTRODUCTION

The process by which water or other volatile substance is removed from a relatively non-volatile material by vaporization, through the application of heat for the purpose of concentration or crystallization, is called evaporation. Evaporation may take place either in the presence or in the absence of air or other gases. In the presence of air, vaporization takes place below the boiling temperature of the solution. Most commercial evaporation processes take place at the boiling temperature in the absence of gases.

**Source of Heat.** — The heat may be applied in many ways. In the first place, heat may be derived from the sun's rays, as in solar ponds. It may be obtained from direct fire under open kettles, as in the old process of making brown sugar, or the present day process of making maple sugar. Steam may supply the heat to submerged coils, or jacketed kettles. In this case, steam is condensed, giving up its latent heat to the solution, which boils and evaporates as a result.

Evaporation is sometimes accomplished by passing highly heated gases through a solution, as in concentration towers. Here, owing to the partial gas pressure, the vapor pressure is lowered, and the boiling temperature drops correspondingly.

The process may be carried on in the open, i.e., at atmospheric pressure; it may proceed under pressure as in steam boilers; or it may be under vacuum, which means under a pressure below that of the atmosphere, in which case it becomes necessary to condense the outgoing vapor and maintain the vacuum by some means. All of these find application commercially.

**Use of Steam.** — With the exception of boilers and a few isolated processes, such as the concentration of caustic in pots,

59

evaporation is accomplished by the use of steam, which condenses on one side of the heating surface, while a corresponding amount of vaporization takes place on the other side.   In fact, in the vast majority of cases, exhaust steam is used for this purpose, having already given up part of its heat in power generation on its way from the boilers.

Steam used outside of power generation is usually called "process steam." By combining power generation with process heat requirements, the cost of the two is very much reduced from what it would be if they were independent.   This development has assumed greater and greater importance in view of the present day high steam pressures, and offers large possibilities. It is really the basis of success in many modern plants.   Outstanding examples are the paper industry, and the sugar industry.

Cost. — The elements of cost which enter into the operation of an evaporator may be divided into two groups, operating costs and fixed charges.   The principal item in operating costs is always the fuel consumption, while the fixed charges depend chiefly on the cost of the evaporation installation and its rate of depreciation.   As a general rule, fuel costs become relatively smaller as the size of the equipment increases, while fixed charges increase.   There is always a point where the total cost is a minimum.   This is the proper size of equipment to use.   This is shown in the diagram (Fig. 19).
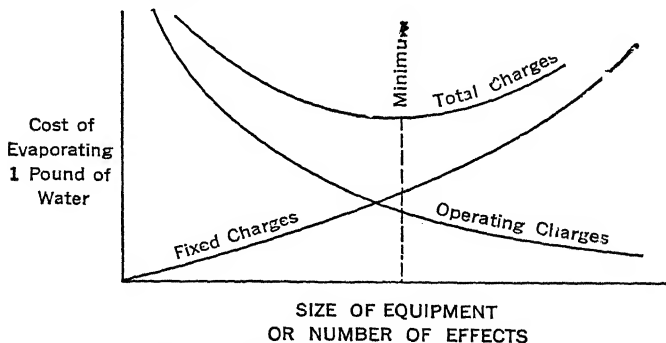


FIG. 19.   Cost Versus Size of Equipment.

## BASIC PRINCIPLES

The discussion herein will be limited to steam evaporation, i.e., apparatus in which the work is done by the use of steam.

**Elemental Evaporator.** — An elemental evaporator consists of two closed spaces separated from one another by a thin metal division, usually in the form of tubes. On one side, steam is being condensed, giving up its latent heat, while on the other, a solution absorbs this released heat by liberating its water through vaporization at a lower temperature and pressure, and it is this difference of temperature that causes the flow of heat through the thin metal division or heating surface.

**Latent Heat of Steam.** — The amount of heat liberated by each pound of steam, as it condenses, is its latent heat at the temperature or pressure existing in the steam compartment. This is subject to some variations as shown in steam tables. For moderate temperature ranges, the value of latent heat is in the neighborhood of 1000 B.t.u. per pound of steam condensed.

The amount of heat required to evaporate one pound of water is its latent heat at the temperature corresponding to the pressure or vacuum under which evaporation takes place, providing the temperature of the solution being evaporated is at the boiling point when it enters the evaporator. If such temperature is below the boiling point, then, to effect the evaporation of one pound of water, sufficient heat must be added to raise the solution to its boiling point, in addition to the latent heat as mentioned above. If, on the other hand, the incoming solution is above the boiling temperature in the evaporator, then, as it enters, there will be a certain amount of self evaporation or "flash," as the temperature drops to correspond to that of the boiling liquid, determined by the vacuum or pressure existing in the liquor space. This will reduce the required amount of heat per pound of evaporation by the value of these extra B.t.u.'s.

The above facts are used in all evaporator calculations, and are of fundamental importance. It will be noted that no mention has been made of any particular temperature or pressure, since, under varying conditions, evaporators do operate through quite a wide range, both as regards temperature levels, and temperature differences.

**Multiple Effect Evaporator.** — It should therefore be very easy to understand how it is possible to take the vapor leaving one evaporator, and use it as steam in another, if the temperature level is simply lowered sufficiently to provide an adequate

working difference.   This is generally known as *multiple effect evaporation*.   Not only is it possible to operate a second evaporator with vapors from the first, but further compounding is used, making a whole series with a number of units, each deriving its heat from a preceding one at a higher temperature.   As many as twelve in a set have been used.   This scheme is usually credited to Norbert Rillieux, an American born of French parents, who, about 1830 promulgated what he termed his *first* and *second principles* of evaporation and heating (see Fig. 23).

**Rillieux's Principles.** — Rillieux's First Principle states that in a Multiple Effect Evaporator, each pound of steam supplied to the first body will evaporate one pound of water in each body of the series.

Rillieux's Second Principle is as follows: If vapors from the various bodies of a multiple effect are used for heating operations instead of steam, the saving so accomplished is equal to the amount of vapors so utilized multiplied by a factor indicating the position of the body in the set, and divided by the total number of bodies.

After elaborate checking, it has been found that the First Principle errs considerably due to heating and flashing, and the variation in the value of latent heat.   The Second Principle, however, gives results that are only very slightly in error, and can be used with fair accuracy.   It is rather surprising that the First Principle was given general recognition very early, but that the more accurate Second Principle was overlooked until rather recently.   Very large additional steam savings have been obtained by the use of the Second Principle after the possibilities of the First Principle were practically exhausted.

Evaporator calculations using Rillieux's Principles are very simple indeed, and are even now used extensively by many engaged in this work for that reason.   Most of the current textbooks use this method exclusively.   It is far better to make a heat balance in which the flow is fully accounted for, representing facts beyond question.   The method used will be elaborated later.

**Heat Transmission.** — The transmission of heat through the surfaces of evaporators is a rather complicated process due to the fact that it depends on so many factors, and it is usual to be

guided by established practice rather than theory. It will be attempted to outline briefly at least some of the important points.

The heat transmission, usually indicated by the symbol $H$, is expressed as B.t.u.'s transmitted per square foot of heating surface per hour, and per degree of Fahrenheit difference of temperature between the two sides of the heating surface.

*Conductivity of Metals.* — In the first place, the conductivity of the material making up the heating surface as well as the thickness of the metal must be considered. The conductivity, expressed as $k$, is given in B.t.u.'s transmitted per square foot per hour per degree F. difference between the two sides of the metal, presuming this to be one foot thick. For the metals used in this work, $k$ has the following values: aluminum, 85; yellow brass, 55; copper, 238; wrought iron, 40; nickel, 32. This means that if tubes of these metals were made 1/16″ thick, the transmission would be 192 times the values mentioned above. For copper, this would give 45,696 B.t.u.'s per sq.ft. per hr. per degree. The highest figure we have on record, for evaporators under ideal conditions, perfectly clean, is about 2000. It is therefore evident that many important factors are lacking in the above.

*Resistances to Heat Flow.* — It has been found that the resistance to the flow of heat through the metal wall is but a very small part of the total. There is a very material resistance offered to the passage of heat through what is called the steam film, or the crossing of the small layer of water on the steam side of the heating surface before the heat enters the metal. This is greatly aggravated if the steam being condensed has a small proportion of air or non-condensable gas present.

Then, on the liquor side, heat has to leave the metal of the tubes and go through the liquor film on that side also, and at this point is encountered by far the greatest resistance to heat flow, for not only must the liquid film be traversed, but also, the inevitable accumulation of scale, corrosion, or deposits as well.

The normal heat transmission obtained in practice for multiple effects ranges in the neighborhood of 200 to 400 as a result of the above mentioned unavoidable impediments. Below are mentioned some of the factors making up these, and thus affecting the heat transmission:

1. Cleanliness of heating surface,
2. Temperature of steam,

3. Rate of evaporation,
4. Hydrostatic heads,
5. Viscosity of solution being evaporated,
6. Non-condensable gases.

In estimating the probable heat transmission, more than in any other feature, it is necessary to be guided almost entirely by practice, and ample allowance must be made for possible local variations.

The accompanying Fig. 20 shows the heat transmissions now being obtained in the Sugar Industry with the better designs of
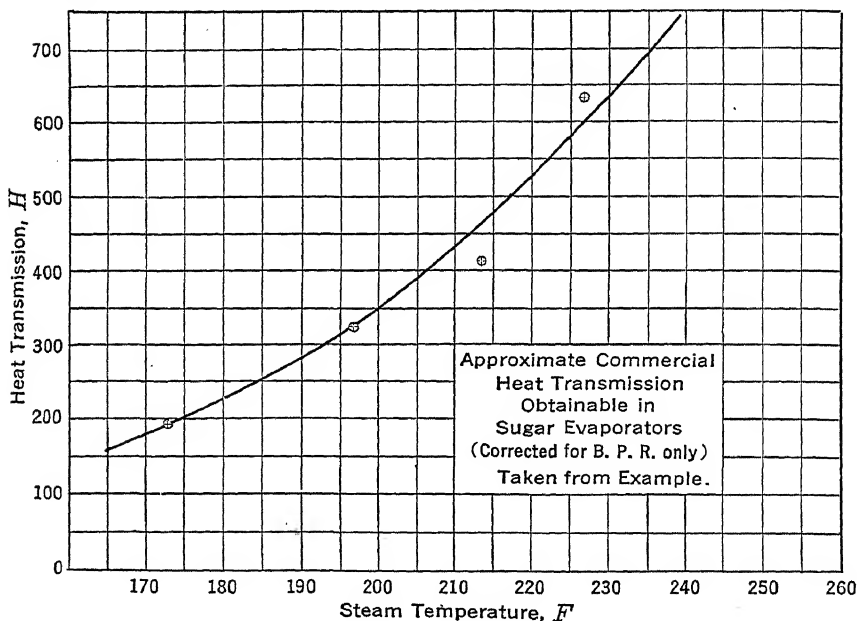


FIG. 20.   Approximate Heat Transmission Obtainable in Sugar Evaporators.
(Corrected for B. P. R. only.)

evaporators.   Isolated units give better than shown, and many give much less, perhaps 60 per cent of the given ratings.   This curve may be used in working up fairly good examples.

**Boiling Points of Solutions.** — There is a direct relation between the boiling temperature of water and the pressure under which this takes place.   This very important relation is fully

brought out in steam tables. For instance, at atmospheric pressure, water boils at 212° F.; at 10 lbs. gauge pressure, the temperature is 240° F.; at 100 lbs., it boils at 338° F.; and at 1000 lbs., the temperature attained is 546°. Below atmospheric pressure, the temperatures go down correspondingly. Under 10″ vacuum, the temperature is 192° F.; at 20″, 162°; and so on. At 29.74″ vacuum, water boils and freezes at the same time, and this is one of the commercial processes of refrigeration.

The presence of solids dissolved in water raises the temperature at which it boils. This increase depends upon the amount in solution, and also upon the chemical composition. Raoult's law, bearing on the subject, states that the effect of dissolved solids on the boiling point of water at atmospheric pressure for dilute solutions of simple substances, which, like sugar dissolve in water without reacting with it, or without being dissociated by it, may be given by the following formula:

*The Boiling Point Rise* (B.P.R.) = 51.5 $n$, in degrees F., where $n$ is the mol fraction of the solid in solution, that is, the mols of solid divided by the sum of the mols of solid and water. For other solutions, experimental data are necessary.

As an illustration, a saturated solution of common salt, NaCl, has a B.P.R. of 15.8° F., and therefore boils at atmospheric pressure at 227.8° F. For any other pressure or vacuum, the boiling point is obtained by simply adding this B.P.R. to the temperature of steam at that particular pressure or vacuum.

*Abnormal Boiling Point Rise.* — Actually, in practice, this B.P.R. for a given concentration is usually higher than the tables indicate, owing to a very peculiar phenomenon having to do with the speed at which vapor is released from the boiling surface. This phenomenon has been encountered on two separate occasions where conditions as to rate of ebullition were favorable to it. In both cases, the evaporator was provided with mechanical circulation, and no evaporation took place in the tubes, but rather by flashing at the boiling surface. In one instance, the unit was equipped with 13,000 sq.ft. per body, the tubes being 2½″ diameter, and six feet long. In the other, it was a pilot unit, having only seven square feet, the tubes being 1¼″ diameter by four feet long. In the large unit, which was a triple effect, the B.P.R. as determined by careful laboratory experiments, was 20.5° for the first effect; 18.0° for the second; and 16.0° for the third. In all cases, the solution was pre-

cipitating salts.   Actually, on the evaporator, the B.P.R.'s were 30.6°, 30.7°, and 31.5°, respectively, or an increase over theoretical of 10.1°, 12.7°, and 15.5°, respectively.   The evaporator was run "counter current," with feed in the order of 3–2–1. The bodies of this evaporator were 22'0" diameter.

In the case of the small unit, there was only one body, so arranged that it could operate as a first, second, or third effect. The solution treated consisted of a mixture of sodium chloride and sodium sulfate which had to be separated.   The method was to crystallize out the salt by evaporation, and the sodium sulfate by cooling.   In all tests, saturation obtained, and the theoretical boiling points were all carefully determined by laboratory experiments.   Space does not permit full elaboration, but it can be said that in every instance, the B.P.R. was greater than the theoretical.   The largest discrepancy occurred in the last effect under 28" vacuum, where the specific volume of vapors was the greatest.   In order to attempt an explanation, four different speeds were tried with the following results:

| Speed of Vap. Release, Ft./sec. | Vapor Temp. | Theor. Boil. Temperature | Actual Observed Boil. Temperature | Abnormal B.P.R. |
|---|---|---|---|---|
| 7.70 | 101 | 117 | 134 | 17 |
| 10.95 | 101 | 117 | 146 | 29 |
| 14.10 | 101 | 117 | 156 | 39 |
| 17.95 | 101 | 117 | 164 | 47 |

These two examples show how dangerous it is to go too fast on insufficient information.   It also shows that after all it pays to make sure, and not trust too much to data obtained on small scale laboratory apparatus.   It is true that the ratings on the experimental evaporator were purposely exaggerated to bring out the facts more emphatically.

Radical evidence of the phenomenon as outlined above has not been found in evaporators having natural circulation, and a possible explanation is that with natural circulation, and evaporation taking place in the tubes, the vapor liberating area is many times what it would be where it is presumably limited to approximately the cross section of the evaporator body.   It might be interesting to state that abnormal B.P.R.'s were also observed in operating this experimental unit on pure water.

Solids in suspension will also increase the B.P.R.; it is possible

to raise the boiling point of water in a simple laboratory experiment by maintaining a certain amount of clay in agitation in a beaker being heated by a Bunsen burner.

**Static Head.** — It has been carefully brought out that as the pressure increases, the temperature at which ebullition takes place also increases. If the heating surface of an evaporator is below the boiling level of the solution being evaporated, the boiling temperature will rise due to the additional hydrostatic head, just as if the pressure had been increased, which it actually has.

With very few exceptions, all evaporators have to operate with a certain amount of this temperature loss. It is the prime object of all good designers so to plan their apparatus that this unavoidable handicap will be reduced to a minimum. The only evaporator to our knowledge free from hydrostatic head loss is the Lillie design, in which the solution being evaporated is sprayed on the tubes, which as a consequence are never really submerged, but merely covered with a thin film, hence the name "film evaporator." The expense and complication incident to such mechanical circulation has limited its use, and only very few manufacturers have adopted it.

A given hydrostatic head involves a larger temperature loss as the vacuum is higher, or the pressure less, for given increments of pressure correspond to larger and larger temperature changes as will be readily seen by reference to a steam table. The accompanying chart (Fig. 21) gives a good idea of this feature. In this case, vapor temperatures are plotted as abscissae, and increase of boiling point for various heads as ordinates. These heads are all based on a solution having a specific gravity of unity. If it is greater than unity, corresponding corrections must be made.

In order to obtain the real value of the heat transmission in an evaporator, it is evident that besides the B.R.P. due to the concentration of solids, a further reduction of gross temperature difference between the two sides of the heating surface must be made, corresponding to the hydrostatic head loss as explained above.

This means more and more complication. After all, if an evaporator suffers from excessive hydrostatic head loss due to faulty design or operation, it is the fault of the design or the operator, and not that of the liquor, so it has been common practice to omit this correction on the assumption that it is part

of the cost of operating an evaporator. With mechanical cir-
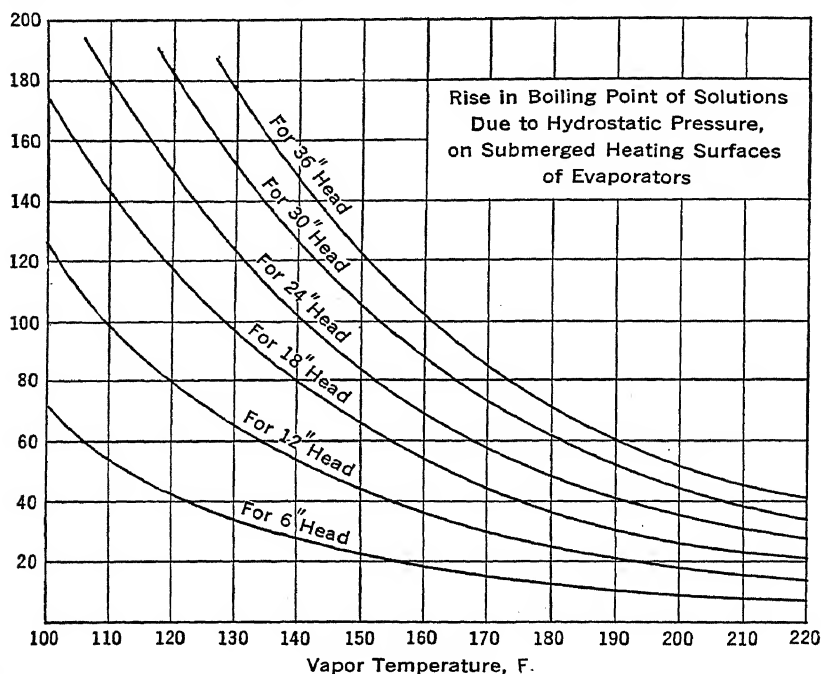culation, an entirely different condition obtains, which is elab-



Rise in Boiling Point of Solutions
Due to Hydrostatic Pressure,
on Submerged Heating Surfaces
of Evaporators

For 36" Head
For 30" Head
For 24" Head
For 18" Head
For 12" Head
For 6" Head

Vapor Temperature, F.

FIG. 21.    Rise in Boiling Point of Solutions Due to Hydrostatic Pressure on
Submerged Heating Surfaces of Evaporators.

orated under that heading. For scientific analysis, however, full
consideration should be given to this important factor.

**Viscosity.** — Probably the greatest deterrent factor in the
operation of evaporators is viscosity. Increase in viscosity
causes the solution to become sluggish, and more and more
difficult to move rapidly, a condition of prime importance for
efficient heat transmission.

When it is necessary to attain high concentration, if the vis-
cosity is too great, the problem can be made much easier by
carrying the highest concentration in the body of the evaporator
having the maximum temperature, for viscosity decreases very
materially with increased temperature.

If excessive viscosity obtains in a multiple effect, the inevitable

result will be loss in capacity, and it is sometimes advantageous to sacrifice a little steam economy by doing the finishing in a separate small single effect evaporator operating on a large difference of temperature, p e r m i t t i n g the large unit to carry on the major part of the work at a reasonably normal capacity. Mechanical circulation is also a great help in overcoming this difficulty, but it is expensive in first cost, and cost of operation. The published data on the isolated effect of viscosity in evaporators is very incomplete. T h e attached graph (Fig. 22) shows in a general way how heat transmission is affected by this feature.

**The Heat Balance.—** It has previously been indicated that evaporator calculations made up according to Rillieux's Principles do not give accurate r e s u l t s, and
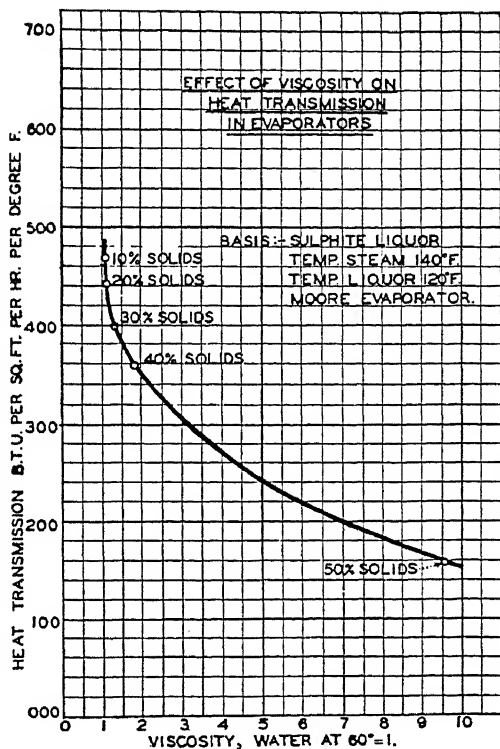


FIG. 22. Effect of Viscosity on Heat Transmission in Evaporators.

that to get a closer approximation to the truth it is necessary to resort to a true heat balance. The problem is usually presented in such a form that the unknown is the steam consumption for a given load. The mathematical processes required to arrive at this figure accurately are so involved that they are not used. The method of procedure is by trial and error, and this will be illustrated in the following discussion.

*Parallel Flow Feed.* — Multiple effect evaporation as a rule is a continuous process, the solution entering the first body of the set, and passing successively into the next in the series, finally leaving

the last body at ultimate concentration. It is customary to number the bodies of the multiple evaporator serially, calling the unit receiving the steam the first effect. Occasionally, for special reasons, each body is fed independently with the original solution. This is usually the case in the manufacture of salt from saturated brine.

In the concentration of soda and sulfate liquors in paper mills, the solution enters the second body, and proceeds in normal sequence to the last, whence it is pumped back to the first for final concentration. The reason for this is that at ultimate density, the viscosity is so great as to make satisfactory operation very difficult. By resorting to the feed sequence above, the ultimate concentration takes place at the highest temperature, thus reducing the retarding effect of viscosity, which is decreased by the higher temperature, and normal capacity can be obtained without excessively large heating surfaces. (See discussion on Viscosity.)

*Counter Current Feed.* — For certain work, it is advisable to run *counter-current*, introducing the solution into the last effect, and pumping back to the preceding one, finally reaching the first body, where ultimate concentration takes place. Potash-bearing brines are usually handled in this way, in order to keep the potash salts in solution while the other undesirable salts are crystallized out by evaporation at increasingly higher temperatures, thus retaining the more soluble potash salts in solution.

**Evaporator Problems.** — As a typical evaporator problem, the following is given from the familiar Sugar Industry:

Concentrate 100,000 lbs. per hour of cane juice from 15 per cent solids to 60 per cent solids in a quadruple effect, steam being available at 5 lbs. gauge pressure, vacuum being maintained at 26″. The temperature of the incoming juice is at 180° F.

In the first place, the percentage of evaporation by weight is expressed as the ratio of the difference of the per cent solids to the final per cent solids, or in this case

$$\frac{60 - 15}{60} = .75, \text{ or } 75 \text{ per cent.}$$

The amount of evaporation is therefore 75,000 lbs. per hour.

*Temperature Drops.* — The distribution of temperature drops through the evaporator must next be determined. This is by

far the most difficult problem, as it is affected by so many factors. However, in the Sugar Industry, after much practice and observation, we have found that an equal division of pressures among the various bodies just about corresponds to normal operating conditions. Since one pound pressure is about equal to two inches of mercury, the total pressure drop across the quadruple is $(5 \times 2) + 26 = 36''$. Since there are four bodies, then, the pressure drop through each will be $9''$ of mercury.

*Boiling Point Rise.* — In order to obtain the boiling point rise in each body, it is necessary to know the concentration. This can be obtained by tentatively assuming that the evaporation is equally divided among the various effects. This results in, for the first effect, 18.5 per cent solids; for the second, 24 per cent; for the third, 34.3 per cent; and for the fourth, the final concentration, or 60 per cent. The B.P.R.'s corresponding to these densities are from the tables, 0.50°, 0.75°, 1.50°, and 5.6°. However, cane juice is being evaporated, and not pure sucrose, which is slightly different. The actual B.P.R.'s as observed in practice are 0.5°, 1.0°, 2.0°, and 9.0°.

The distribution of pressures and temperatures in this quadruple effect is therefore as follows:

| Nomenclature | Steam Belt 1 | Vapor Belt 1 | Vapor Belt 2 | Vapor Belt 3 | Vapor Belt 4 |
|---|---|---|---|---|---|
| Vacuum or pressure........ | 5.0 lbs. | 0.5 lbs. | 8.0″ v. | 17.0″ v. | 26.0″ v. |
| Steam and vapor temp...... | 227.0° | 214.0° | 197.0° | 173.0° | 125.0° |
| Boiling point rise......... | | 0.5° | 1.0° | 2.0° | 9.0° |
| Boiling point............. | | 214.5° | 198.0° | 175.0° | 134.0° |
| Latent heat at steam or vapor temperature............. | 960.7° | 969.1° | 979.7° | 994.0° | 1021.6° |

*Simplifying Assumptions.* — Before proceeding with the Heat Balance, it might be well to state some of the simplifying assumptions which are made as follows: 1. It is assumed that the heat contained in the vapors leaving the liquor correspond to the latent heat of steam for the pressure or vacuum existing. Where there is a very high B.P.R., superheat in these vapors has been observed, but it is so small that correction for this is omitted. 2. Where heating or flashing takes place, theoretically, a correction should be made for the specific heat of the solution. Usually, this is rather small, and the specific heat is assumed as

constant at unity.   By this assumption, the heating operations will require more steam, and the flash will release more vapor. Such a correction is easily added if the discrepancy is great enough to make a material difference.

*Heat Balance.* — Below is given the Heat Balance for the problem outlined above.   The quantity of steam, 20,600 lbs. per hour was arrived at by trial and error.   Usually, three trials will give results sufficiently close for practical purposes, say, within

<div align="center">HEAT BALANCE, QUADRUPLE EFFECT.</div>

| Bodies, | Specifications, | Heat, B.t.u.'s | Juice, lbs. |
|---|---|---|---|
| 1. Steam, 20,600 lbs. @ 227 = 20,600 × 960.7 = ........ | | 19,800,000 | 100,000 |
| Deduct for heating juice, 100,000 × (214.5 − 180 = 34.5) = ................................. | | 3,450,000 | |
| Available for evaporation......................... | | 16,350,000 | |
| $L$ @ 214 = 969.1, $E-1 = \dfrac{16,350,000}{969.1} =$ .................... | | | 16,900 |
| Transferred to No. 2............................... | | | 83,100 |
| 2. Vapor from No. 1............................... | | 16,350,000 | |
| Add juice flash, 83,100 × (214.5 − 198 = 16.5) = .... | | 1,370,000 | |
| Available for evaporation......................... | | 17,720,000 | |
| $L$ @ 197 = 979.7, $E-2 = \dfrac{17,720,000}{979.7} =$ .................... | | | 18,100 |
| Transferred to No. 3............................... | | | 65,000 |
| 3. Vapor from No. 2............................... | | 17,720,000 | |
| Add juice flash, 65,000 × (198 − 175 = 23) =........ | | 1,495,000 | |
| Available for evaporation......................... | | 19,215,000 | |
| $L$ @ 173 = 994.0, $E-3 = \dfrac{19,215,000}{994.0} =$ .................... | | | 19,350 |
| Transferred to No. 4............................... | | | 45,650 |
| 4. Vapor from No. 3............................... | | 19,215,000 | |
| Add juice flash, 45,650 × (175 − 134 = 41) =........ | | 1,870,000 | |
| Available for evaporation......................... | | 21,085,000 | |
| $L$ @ 125 = 1021.6, $E-4 = \dfrac{21,085,000}{1021.6} =$ .................... | | | 20,650 |
| Finished concentrated syrup........................ | | | 25,000 |

*Note:* The above figures are to slide rule accuracy.

200 lbs. of the amount of evaporation required. It is interesting to find that as calculated by Rillieux, the steam requirements would have been 75,000/4 = 18,750 lbs. per hour, or about 10 per cent too low.
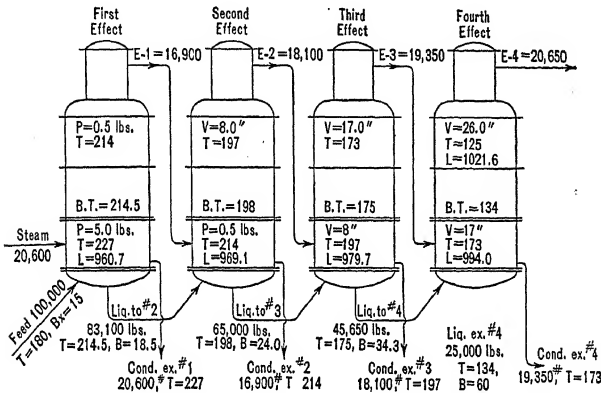


DIAGRAMMATIC SKETCH OF QUADRUPLE EFFECT

Fig. 23. Diagrammatic Sketch of Quadruple Effect.

Figure 23 is a diagrammatic sketch showing the quadruple effect with the operating conditions all fully indicated, with quantities, vacua, and pressures all shown.

Figure 24 shows to scale, as ordinates, the steam consumption
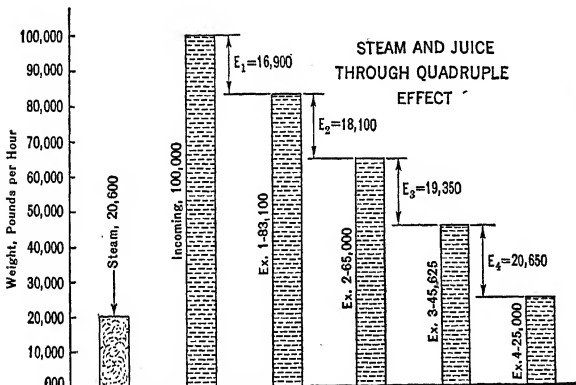


Fig. 24. Steam Consumption and Evaporation in Quadruple Effect.

in pounds per hour, as well as the weight of liquor entering the apparatus, and as it leaves each body, the shrinkage of weight representing the evaporation in each case.

*Distribution of Vacua, Temperature and Pressure.* — The accompanying diagram (Fig. 25) shows the distribution of vacuum,
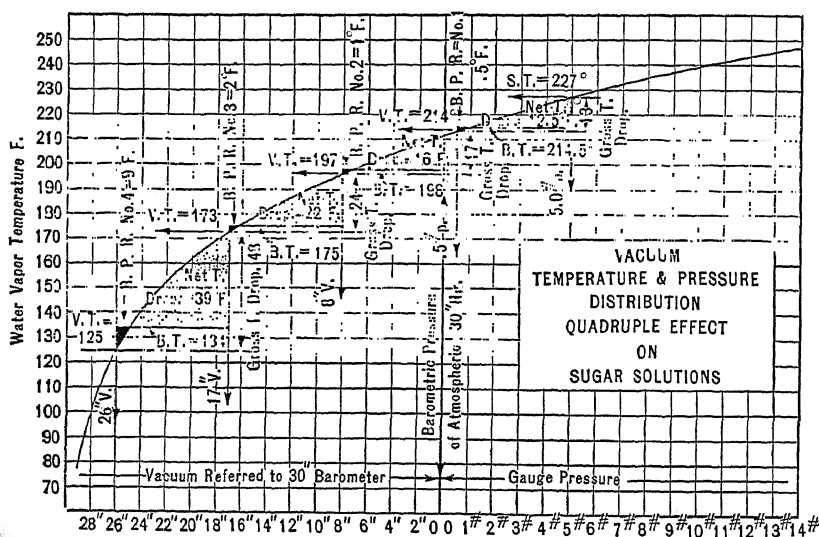


FIG. 25.  Vacuum Temperature and Pressure Distribution in Quadruple Effect.

temperature, and pressure for the problem analyzed.  The ordinates represent temperatures, and the abscissae, pressures expressed as pounds gauge, i.e., above the atmosphere; and vacua, in inches of mercury.   Vacuum is the difference between the pressure of the atmosphere and a lower pressure in a closed container, such as an evaporator.   The pressure of the at- mosphere is 14.7 lbs. per sq. in., corresponding to a column of mercury about 30″ high.  This atmospheric pressure is not fixed, but varies with the elevation above sea level and changes in the weather through moderately small limits.

Marks and Davis Steam Tables have been used throughout, and in such tables, all pressures are given as "absolute pressures," which simply means that to the ordinary guage pressures have been added the atmospheric pressure.   When the pressures are given in inches of mercury, they also are "absolute inches."   To

convert a given vacuum reading into " absolute inches," subtract the vacuum reading from the observed barometric pressure.

In making up this chart, vacua and gauge pressures are plotted directly. The operating conditions are all shown. Note how the B.P.R.'s rob the operating temperature differences, leaving the balance as "net temperature drop," or the difference of temperature between the two sides of the heating surface. It is significant to observe that these "net drops" of temperature are greater as the pressure is reduced or the vacuum increased, which is the same as saying that the temperature of steam is lowered.

*Heat Transmitted.* — In practice, a well designed evaporator to carry the load outlined above would have 10,000 square feet, the surface being equally divided between the four bodies, or 2500 square feet each. With the above data, it is easy to calculate the heat transmission as shown below. The quantities of heat indicated in the second column are the amounts of heat actually transmitted by the heating surface, and are taken from the Heat Balance shown previously above. In these amounts, the flashed heat is not included since it does not go through the surfaces.

| Body | Heat Transmitted per Hour | Heat Transmitted per per sq. ft. per hr. | Net Temp. Drop | Heat Transmission | Steam Temp. |
|---|---|---|---|---|---|
| 1 | 19,800,000 | 7,920 | 12.5 | 633 | 227 |
| 2 | 16,350,000 | 6,540 | 16.0 | 409 | 214 |
| 3 | 17,720,000 | 7,090 | 22.0 | 322 | 197 |
| 4 | 19,215,000 | 7,680 | 39.0 | 197 | 173 |

The values of heat transmission would naturally be much greater with water, due to the reduced viscosity, which is quite noticeable in the last body of sugar evaporators. The other factors have also great bearing. This is a safe commercial rating, and allows for normally fouled heating surfaces, and fair operation. It is possible with excellent operation to increase the rating perhaps 20 per cent, but that is about the limit.

*Flow of Total Heat.* — In order to complete the picture of this evaporator operation, it is necessary to go one step further. Your attention is called to the tabulations showing the flow of total heat above 32° through the system. This is supplementary to the Heat Balance, and shows in good detail what becomes of

FLOW OF TOTAL HEAT ABOVE 32° F. PER HOUR THROUGH QUADRUPLE
IN EXAMPLE

*0. Heat Entering Evaporator*
 *A.* Steam, 20,600 × ($H$ @ 227 = 1155.8) =................. 23,800,000
 *B.* Heat in juice, 100,000 × ($h$ @ 180 = 147.88) =.......... 14,880,000
                       —————
  Total............................................. 38,680,000

*1. Heat Leaving First Effect*
 *A.* Heat in condensate, 20,600 × ($h$ @ 227 = 195.2) =...... 4,020,000
 *B.* Heat in vapor, 16,900 × ($H$ @ 214 = 1151.1) =......... 19,450,000
 *C.* Heat in juice, 83,100 × ($h$ @ 214.5 = 182.5) =.......... 15,170,000
                       —————
  Total heat leaviug first effect........................ 38,640,000
  Minus heat in condensate (*A*)........................ 4,020,000
                       —————
  Heat admitted into second effect...................... 34,620,000

*2. Heat Leaving Second Effect*
 *A.* Heat in condensate, 16,900 × ($h$ @ 214 = 182.0) =...... 3,075,000
 *B.* Heat in vapor, 18,100 × ($H$ @ 197 = 1144.6) =......... 20,700,000
 *C.* Heat in juice, 65,000 × ($h$ @ 198 = 165.93) =........... 10,800,000
                       —————
  Total heat leaving second effect....................... 34,575,000
  Minus heat in condensate (*A*)........................ 3,075,000
                       —————
  Heat admitted into third effect....................... 31,500,000

*3. Heat Leaving Third Effect*
 *A.* Heat in condensate, 18,100 × ($h$ @ 197 = 164.93) =...... 2,985,000
 *B.* Heat in vapor, 19,350 × ($H$ @ 173 = 1134.9) =.......... 21,950,000
 *C.* Heat in juice, 45,650 × ($h$ @ 175 = 142.87) =........... 6,520,000
                       —————
  Total heat leaving third effect........................ 31,455,000
  Minus heat in condensate (*A*)........................ 2,985,000
                       —————
  Heat admitted to fourth effect........................ 28,470,000

*4. Heat Leaving Fourth Effect*
 *A.* Heat in condensate, 19,350 × ($h$ @ 173 = 140.87) =...... 2,435,000
 *B.* Heat in vapor, 20,650 × ($H$ @ 125 = 1114.5) =.......... 23,050,000
 *C.* Heat in juice, 25,000 × ($h$ @ 134 = 101.88) =........... 2,550,000
                       —————
  Total heat leaving fourth effect....................... 28,035,000

*5. Heat Leaving Quadruple Effect*
 *A.* Heat in condensate 1-*A*..................... 4,020,000
  Heat in condensate 2-*A*..................... 3,075,000
  Heat in condensate 3-*A*..................... 2,985,000
  Heat in condensate 4-*A*..................... 2,435,000
                   —————
  Total................................... 12,515,000 12,515,000

$B.$ Heat in vapor to condenser, $4\text{-}B$...................... 23,050,000
$C.$ Heat in juice, $4\text{-}C$................................. 2,550,000

Total heat leaving quadruple effect.................... 38,115,000
Heat input, see 0 above.............................. 38,680,000

Accumulated slide rule error.......................... 565,000

the heat. This information is plotted graphically to scale in Fig. 26.
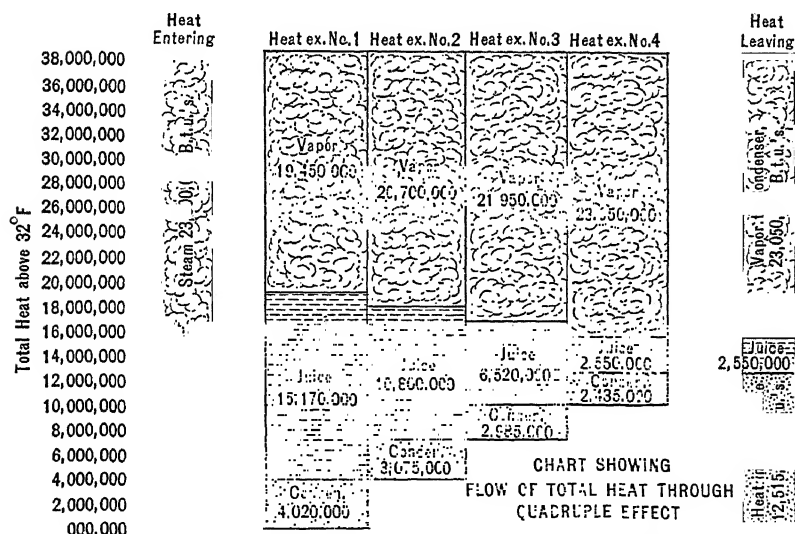


FIG. 26. Flow of Heat through Quadruple Effect.

In the first place, it must be remembered that heat enters the evaporator in the juice as well as in the steam, as shown in the first ordinate. It should be especially noticed that the heat above 32 in juice is almost 2/3 as great as the heat contained in the steam used.

Leaving the first effect, heat appears in vapor (steam), juice, and condensate. Heat in vapor in this case is less than it was in steam because part of it has been transferred to condensate, and a much larger part has been used to bring up the temperature of juice from 180° F. to 214.5. In fact, the juice has absorbed so much heat, that even though a large part of it has been evaporated, still, the balance contains more heat than the original.

Heat in the condensate leaving the compartment does not proceed to the next body, but is returned, presumably to the boilers for feeding.

Upon leaving the second body, there are some interesting developments. The heat in the condensate is lost to the evaporator by being removed as such. The heat in juice is very much less, for not only has there been evaporation, and therefore loss of weight, but the temperature has also gone down. The heat in vapor has materially increased, principally due to "flashing," or self evaporation, as juice dropped in temperature due to reduced pressure and, this flash is added to the vapor. The heat leaving the third effect follows the same characteristics as that leaving the second, and with the fourth body the same general trend can be observed.

Analyzing the final results, there are very interesting data. The vapor leaving the quadruple has almost as much heat as contained in the original steam, in spite of the losses in condensates. This has happened at the expense of heat in the juice, which has dwindled down to about 1/6th of its original value due to reduction in weight of four to one by evaporation, and in temperature from 180° to 134° due to lowered boiling point caused by increased vacuum in the last body. The total heat in the sum of the condensates has increased until it amounts to about 80 per cent of the heat originally contained in the juice.

In order to save the waste of heat in the condensates of the second and third effects, these waters are sometimes flashed successively into the steam compartments following, thus lowering the water temperature, and recovering some of the otherwise lost B.t.u.'s. This gain is really very small. In the Sugar Industry, sometimes, the condensates are used on a heat exchanger to warm up cold juice.

**Vapor Heating.** — In the discussion of Basic Principles, mention was made of use of vapors robbed from the various bodies of multiple effects for heating solutions instead of doing this operation with steam, all of which was originally incorporated by Rillieux in his Second Principle defined in the above reference.

A careful heat analysis of this matter provides a better definition of the added economies thus: The saving of heat by the use of vapors from bodies of a multiple effect for heating operations is equal to the total amount of latent heat in the vapors

withdrawn, less the heat cost of replacing the evaporation which would have been accomplished by their use in the apparatus had they not been withdrawn. It follows, that where vapors are used which would normally go to the condenser, the saving is 100 per cent of the heat utilized, and becomes less and less as we move back towards the steam end of the apparatus.

*Terminal Difference.* — In order to effect the saving, the temperatures must be such as to permit it. In these operations, it has been easily possible in practice to heat solutions within 10 degrees of the temperature of the vapor used. This is called the terminal difference. In order to justify the added complication, the range of heating must be sufficient. For instance, with vapor at 140°, it would not pay to make the installation if the initial temperature of the solution being heated were 125°, as this would only give a rise of 5 degrees, since the maximum temperature attainable at the heater is 10 degrees less than the vapor temperature, or $140 - 10 = 130°$. On the other hand, an initial temperature of 100 degrees, would give a range of 30 degrees, which is worth while. Also, if the operation is on too small a scale, it will not pay. It is a matter of estimating the commercial value of the returns as compared with the total cost of getting them, bearing in mind that no complication should be introduced that does not pay good dividends on the investment.

*Vapor Cells.* — In large scale operations, it has been found that robbing vapors from other than the last bodies of multiple effects involves objectionable complications in the operation, and that it is more advisable to use separate *vapor cells*, i.e., an additional multiple effect all of whose vapors are used for heating operations. This scheme has worked out very well indeed. In order to operate the unit with the smallest possible temperature difference, concentration of the solution to ultimate density is avoided, the partially evaporated liquid joining the feed to the multiple effect equipped with a condenser, where final evaporation is carried on. This gives juice vapors having a higher temperature, and thus makes their availability much greater and more valuable.

Since it is advisable to operate on small temperature differences, the heating surfaces must be ample in proportion, and the evaporator designed to give the maximum possible heat transmission. A good example might be cited of a sugar factory in actual operation having a double effect vapor cell operating on 8 lbs. steam, the vapor leaving the last body at 212°, all going to juice

heaters, where the temperature of the juice is raised from 125° to 210°.

In addition to ample and efficient heating surfaces in the vapor cell, equally good design and operation is required at the heaters, to maintain the smallest possible terminal difference, that is, to heat the juice to as near vapor temperature as possible. In the above example, this terminal difference was only 2 degrees. It has been known to reach practically 0 under particularly favorable conditions.

*Various Sized Bodies.* — If, instead of using a separate vapor cell, as suggested here, vapors are robbed from bodies of the multiple effect, then, it is advisable to rearrange the distribution of heating surfaces in a general way, proportional to the amount of heat to be transmitted through them, and it is quite common to see a multiple effect with various sized bodies, designed as suggested. We might point out that these matters are not very rigid, and that even though the surfaces are not strictly proportional to the transmitted heat, the temperatures will readjust themselves to compensate, and it is unwise to make too many sizes unless there is a radical difference of heat to be transmitted. The old timers used to increase the heating surface of straight multiple effects about 5 per cent in each successive body, but this is not done to-day, as it has been found unnecessary.

*Heat Balance.* — In making up a heat balance where there is robbing of vapors, proceed as in a straight heat balance, and deduct the required juice vapors for heating at the proper point, leaving the balance to proceed to the succeeding body. The distribution of temperatures usually remains approximately the same.

In order to give an idea of the direct results of vapor heating, refer to the example in the discussion of Heat Balance. If we add to this operation the heating of 100,000 lbs. of juice from 100° F. to 212°, the additional steam consumption would be:

$$\frac{100,000 \times (212 - 100 = 112)}{L @ 227 = 960.7} = \dots\dots\dots\dots\dots \quad 11,650 \text{ lbs.}$$

For original quadruple. . . . . . . . . . . . . . . . . . . . . . . . .  20,600 lbs.

Total for heating and evaporation. . . . . . . . . . . . . . . .  32,250 lbs.

On the other hand, if this juice is heated to 205° with vapors from the first effect, the steam consumption of this evaporator will become:

Steam for quadruple effect...................... 29,000 lbs.
Heating to 212 with exhaust steam,

$$\frac{100,000 \times (212 - 205 = 7)}{L @ 227 = 960.7} = \dots\dots\dots\dots\dots\dots\dots \quad 730 \text{ lbs.}$$

Total for heating and evaporation............... 29,730 lbs.

Steam saving by vapor heating instead of using steam directly, is the difference between the above two, or 2,530 lbs. per hour. The interesting part of it is that the heating surface of the quadruple remains the same, 10,000 sq.ft. However, the distribution is changed, the first body having 4000 sq.ft., and the others 2000 sq.ft. each. Another important fact is that the vapor going to the condenser has dropped from 20,650 lbs. per hour to 17,850 lbs. per hour, showing a decreased load on the condenser, and a saving of injection water. It is quite characteristic of these operations that as more vapor heating is resorted to, the load on the condenser is reduced more and more. The heat is absorbed by the cold juice instead of the injection water.

All sorts of vapor heating are extensively used to-day, and have resulted in very large steam economies which have been secured at a very moderate cost.

**Vapor Compression.** — The aggravatingly tantalizing fact about operation of evaporators is that the amount of heat contained in a pound of vapor leaving the apparatus is only slightly less than that of the steam doing the work. This has led to many efforts from the very beginning at adding to this vapor sufficient heat to make it fit for reintroduction to the evaporator as operating steam.

Referring again to the example under the heading of Heat Balance, consider the first body of the quadruple effect in which the temperature of the steam space is 227° F., while the temperature in the vapor space is 214°. The total heats in the two cases are 1155.8, and 1151.1 B.t.u.'s per pound, a difference of only 4.7 B.t.u.'s, or about 0.4 per cent. It would seem that it should be a simple matter to add 4.7 B.t.u.'s to this vapor, and convert it into steam to send back to the same evaporator, as steam.

The problem is not so simple. Merely warming the vapor to bring up its heat contents to 1155.8 simply results in steam at the same pressure, superheated to 237° F., which would most assur-

edly amount to nothing as far as results are concerned.   The only
way to accomplish the desired is to compress the vapor to the
pressure of the original steam.   This compression is adiabatic,
and therefore, the entropy remains constant.   By reference to a
Mollier Diagram, we find that the required heat input would be,
not 4.7 B.t.u.'s, as suggested above, but about 20 B.t.u.'s, and
that the compressed vapor would now be superheated about 40
degrees after having attained the desired pressure of 5 lbs.
gauge, or a temperature of 267° F., with a total heat of 1171
B.t.u.'s per pound.

Operation along these lines is well established.   The com-
pression is accomplished either by mechanical means as in a
turbo-compressor, or it may be done by a steam injector or
thermo-compressor, using live steam for this purpose.   In order
for mechanical compression to pay, the cost of power must be
cheap.   There are many localities in this country and abroad
where power may be obtained at sufficiently low prices to permit
mechanical compression of vapors in conjunction with evapor-
ators.

The conditions under which compression of vapors in evap-
orators is economical are limited.   Due to the excessive specific
volume of steam at relatively low temperatures, the size of the
apparatus becomes very excessive per unit of work done, and
therefore, most operations of this kind are carried on at pressures
at or above the atmosphere.

In the case of a steam injector or thermo-compressor, as an
example, might be taken the operation as outlined above with
live steam at 100 lbs. gauge pressure.   The total heat of steam
at this point is 1188.8.   After adiabatic expansion in the nozzles
to 5 lbs. gauge, or 19.7 abs., the total heat would be 1058, showing
130.8 B.t.u.'s available for the compressed vapor.   The number
of pounds of vapor that can be compressed by the use of this
one pound of live steam will therefore be 130.8/20 = 6.54.   Due
to the proverbial inefficiency of the injector, it may be possible
actually to compress only two pounds of vapor, and an evaporator
using live steam only in such a steam injector would evaporate
about three pounds of water per pound of steam used.

*Mechanical  Compressor.* — With the mechanical compressor,
the efficiency might attain perhaps 50 per cent, and if power is
cheap, the operation will be justified.   On this assumed efficiency
basis, the energy required to compress a pound of steam through

the same range as above, would be

$$\frac{777.5 \times 20}{.50} = 31,100 \text{ foot pounds, or 40 B.t.u.'s.}$$

Since there are 3411.5 B.t.u.'s per K.W.-Hr., the power required per pound of vapor compressed would be the ratio of 40 to 3411.5, or .01173 K.W.-Hr. In other words, one K.W.-Hr. would evaporate roughly 100 lbs. This figure does not include radiation loss, nor the amount of heat required to bring the solution up to the boiling point in the evaporator, all of which must be provided in addition to the electric energy outlined above. By using a heat exchanger between the outgoing water of condensation, and the incoming solution to be evaporated, the additional heat can be very materially reduced.

Certain features must be brought out concerning this cycle of evaporation. In the first place, operation should be by preference with a small difference of temperature across the heating surface of the evaporator, as this will reduce the amount of compression required, and thus lower its cost.

In the second place, as an operating proposition, if a thermo-compressor is used, it cannot be throttled, and should run full speed or not at all. This feature is overcome by using a bank of smaller units, which can be turned on or off one at a time for reduced capacity. The steam nozzles are designed for a certain operating pressure difference, and will not perform efficiently unless these conditions are maintained.

An interesting application of the thermo-compressor is its use on the first body of a multiple effect when there is a shortage of exhaust steam which must be made up by throttling down live steam. Here, the thermo is used as a reducing valve, giving perhaps two pounds of free evaporation with each pound of live steam used, and thus materially helps out the steam economy.

**Circulation.** — Very little is known about the circulation in evaporators. Usually it is said that an evaporator has good circulation, and this opinion is based simply upon visual observation of the agitation going on inside. Nevertheless, it is an important subject, and should be carefully discussed here. By circulation, we mean upward movements of liquid in some parts of the evaporator, accompanied by a corresponding downward movement in other parts. That is to say, the apparatus is so

designed that the ebullition caused by the heating surface in some parts will make the solution rise with the bubbles of vapor, and this liquor, after it has released the bubbles at the boiling surface will return to the bottom of the evaporator for a new circuit.

*Downtakes.* — In upright standard evaporators, this is usually accomplished by making up the surface of a large number of small tubes, and installing a very large one in the center of the body, which is in the shape of a vertical cylinder. Some designs, instead of providing one large central tube, provide a number of small ones. Occasionally some designer will have a segment of tubes left out at the side opposite the steam inlet, and circulation takes place in this segment opening. There are a number of variations all aiming at the same purpose.

In horizontal tube evaporators, a space is left open between the outer tubes and the shell, which serves the same purpose as the large tubes or downtakes as mentioned above.

As far as it has been possible to determine, the real object of circulation is to cause a thorough mixture of the solution being evaporated to prevent local overconcentration. The volume of liquor circulated depends not only upon the design of the evaporator, but upon the levels at which the boiling liquids are maintained in the tubes by the operator.

*Operating Level.* — From years of experience, it has been found that the best level to maintain for maximum work, is that at which the heating surfaces are never allowed to go dry, and no higher. Any increase of height above this point will result in decreased capacity. As an operating level, to avoid excessively critical conditions, it should be carried so that froth covers the tubes perhaps six or eight inches, and no more. The height necessary for this will depend upon the speed of the evaporator, the proportions of the tubes, the cleanliness of the heating surface, and surface tension of the solution, the specific volume of the vapors as determined by their temperature, among other things.

When evaporating a salting solution with natural circulation, the levels must be carried much higher, or the tubes will coat very rapidly with salt. If the level of the liquid is carried too low, the velocity is very sluggish at the lower ends of the tubes, and they will foul rapidly. An interesting fact is that a slow running evaporator will foul very much faster than one which is pushed to maximum capacity. If the level is too low, and the upper

parts of the tubes go dry, some of the solids may bake on the tubes and form an insulating coating difficult to remove.

*Level Controls.* — Many manufacturers equip their evaporators with automatic level controls to insure better operation. These may be of the float type, or by overflow. One fact to be remembered, however, is that the best operating levels will vary with liquor being concentrated, the cleanliness of the surfaces, and the varying rates of evaporation, and the level control does not take care of variations. It is fixed at a compromise point believed to be better than could be maintained by an operator.

Some have circulation controls which regulate the amount of liquor in circulation, letting the excess pass on to the next body, or leave the apparatus in the case of the last effect. Here the levels vary with the conditions which give the best result.

*Heat Transmission.* — The transmission of heat in an evaporator is rather complicated. At the lower part of the tube, heating takes place, and as the solution proceeds on its way up, it soon reaches a point, where due to decreased hydrostatic head, the pressure is reduced to a point corresponding to boiling temperature. From then on, it is all evaporation, with a gradually increased speed until the top of the tube is reached. For this reason, the heat transmission varies greatly throughout the length of the tubes, being minimum at the bottom, and maximum at the top. It is also characteristic of evaporators that the tubes foul the most at the lower ends, and least at the top.

*Mechanical Circulation.* — For crystallizing solutions, mechanical circulation may be said to be practically indispensible. With natural circulation, it is usually impossible to prevent building up of salt crystals upon the heating surface. When adequate mechanical circulation is used, no evaporation takes place in the tubes. Only heating is evident, followed by flashing when the solution reaches the boiling surfaces.

With mechanical circulation, there is very little fouling of the tubes, and the heat transmission is on the whole very much better. Evaporators are especially designed for mechanical circulation, the best consisting of an outside heating element through which liquid is forced with a pump. The speed varies from 5 to 8 feet per second. The faster the speed, the better the heat transmission, almost in direct proportion, but the power also increases tremendously due to added friction, so that a limit is soon reached.

Many large salt evaporators have central downtakes about half the diameter of the evaporator, in which a circulator is installed, built on the order of a ship propeller, and this forces the passage of brine through the tubes.

Providing no fouling takes place, the heat transmission in an evaporator with natural circulation is considerably more than with mechanical circulation, and for that reason, mechanical circulation has not been generally adopted. Also it is always worth something to avoid the inevitable complication and additional expense.

**Entrainment.** — One of the most important precautions to be observed in the operation of evaporators is to guard carefully against loss of liquids being evaporated by entrainment. By this, is meant the ever-present possibility of small drops of liquid being carried over by the vapors and lost in the condensates.

A casual observation of the conditions obtaining in the liquor space of an evaporator while it is in ebullition will reveal that the vapor near the boiling surface is literally laden with what appears to be fine drops of liquid. As a matter of fact, they are usually not drops, but bubbles of almost microscopic proportions, hollow spheres of vapor enclosed by a film envelope of the liquid being evaporated. As such, they present a large bulk compared with their weight, and are therefore easily carried over by the vapor currents. It is evident that the more rapid the velocity of the vapors, the greater the danger of loss. Evaporators running under high vacuum, since the specific volume of steam is much greater, suffer more from this danger than those which operate under pressure, and thus, the worst condition is found in the last body of multiple effects since they are connected to the condenser, and have the highest vacuum. In addition, since the concentration is the highest in the last body, a given weight of liquor carries so much more solids to be lost.

*Foamy Liquids.* — As a corralary, the danger is greatest with vertical tube evaporators when the tubes are long, and of small diameter, since the velocities at the outlet or top ends is greater. On the other hand, long tubes have decided advantages in their ability to break up foam, if the liquor being evaporated exhibits such characteristics. In fact, that is the standard way of evaporating foamy liquors, which in horizontal tube evaporators would surely boil over. Even with standard vertical short tube evaporators, it is sometimes difficult to control foam.

While on the subject of foam, it is characteristic of foamy liquors that they are much more troublesome at low densities than at final concentration, and very often the foaming problem can be solved by feeding concentrated liquor from the last effect to the first, thus increasing the density during the evaporating cycle. Many evaporators have to use this method to attain satisfactory operation under such conditions. Nevertheless, there is an inevitable penalty to pay, for the increased concentration means increased viscosity, and greater B.P.R. throughout the set, both of which materially reduce capacity, not to mention increasing the steam consumption.

*Catchall.* — The method employed to remove small drops of liquor from the vapors leaving an evaporator is by the use of a separator, or a catchall, wherein, through centrifugal action or change of direction, the small bubbles of liquid are made to impinge on wetted surfaces, where they merge into drops of normal size or layers of liquor which drain to the bottom of the separator to be returned to the evaporator by appropriate piping. These drain pipes must be sealed below the level of the liquid, for, due to vapor friction losses, the pressure in the separator is slightly less than that in the evaporator. If the drain were not sealed, then there would be a flow of vapor from the body back to the catchall which would blow the separated liquid back into the vapor currents in the separator with consequent loss (Fig. 27).

Very few of the commercial separators or catchalls sold with evaporating apparatus are more than mere ornaments. Some years ago, the author installed a separator between the catchall of a quadruple effect and its condenser in a large sugar factory. Accurate records were kept, and in three months this new separator caught entrainment losses which had passed through the original catchall to the value of $18,000.00. The cost of the new unit including installation was about $6000.00, showing a return of 100 per cent per month on the investment.

Baffles installed in the vapor space of evaporators well above the froth line are also a great help, since the velocity is slow, and the vapors impinging on these wetted surfaces remove much of the danger of loss. A very simple device is to install two semi-circular baffles on opposite sides one above the other.

Entrainment losses are much harder to prevent as the vacuum is increased, and are sure to become a menace above 26″ unless extra precautions have been taken.
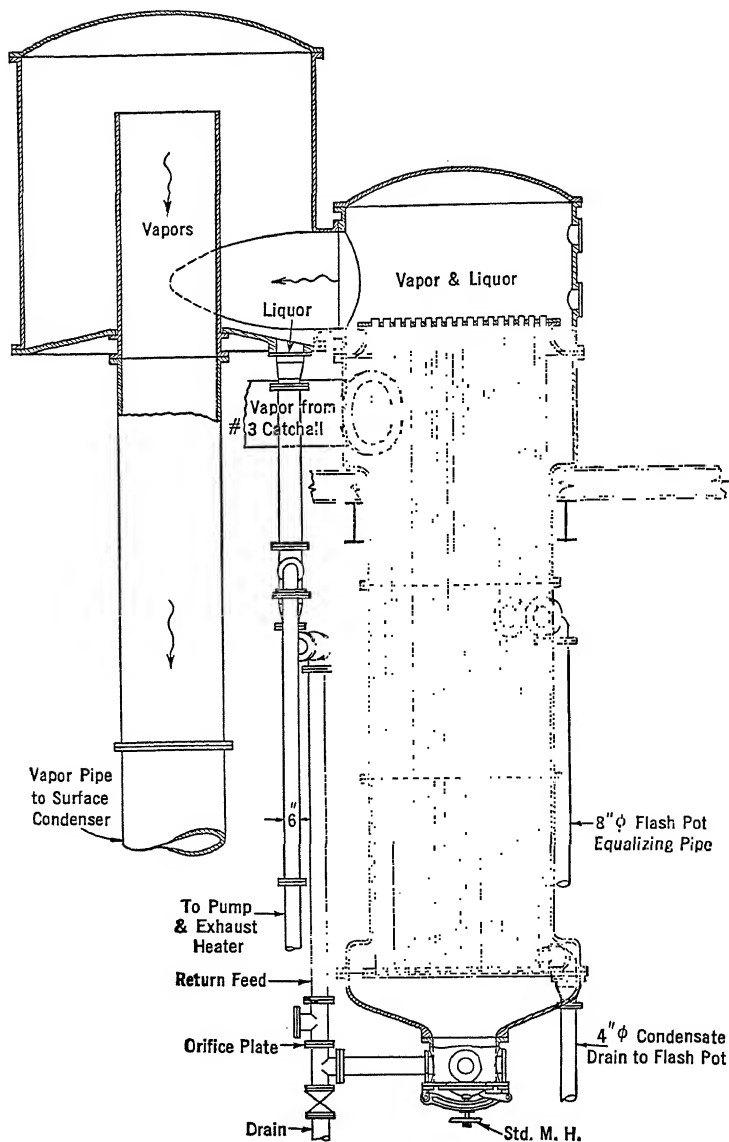
SECTIONAL ELEVATION 4TH EFFECT

FIG. 27.   Sectional Elevation Fourth Effect Showing Catchall.

**Condensers.**[1] — Evaporators operating under vacuum must be provided with condensers whose function is to absorb, into cold water required for this purpose, the heat liberated from the last body.

Either surface condensers or jet condensers are used, according to the requirements. If the vapor being condensed carries contaminating impurities, surface condensers are used when the water must be salvaged, otherwise jet condensers are preferred on account of their smaller cost and reduced upkeep. Both are well known apparatus, and will be discussed briefly here.

*Water Heaters.* — In thinking of condensers, a much better appreciation of their work can be gained by looking upon them as water heaters. A condenser can be considered 100 per cent efficient if it heats the water going through it to the same temperature as the steam or vapor being condensed. In fact, it is perfectly logical to define the efficiency of a condenser as the ratio of the actual rise in the temperature of water going through it to the maximum possible rise. For instance, suppose a given condenser is supplied with cold water at 60° F., and vapor at 125° F., and that the water leaving it is 110° F. Then, the efficiency would be

$$\frac{110 - 60}{125 - 60} = .78 \text{ or } 78 \text{ per cent.}$$

The difference between the temperature of steam being condensed, and outgoing hot water is called the terminal difference, and is used extensively in appraising the work of condensers. In the above example, the terminal difference is 15 degrees.

*Amount of Water.* — The amount of water required by a condenser can be easily calculated. It is merely a matter of absorbing the latent heat of steam or vapor being condensed by raising the temperature of the injection water. In the example above, the value of latent heat at 125° F., is 1021.6 B.t.u. per pound. Each pound of water going through the condenser absorbs 50 B.t.u. since its temperature increases 50°, hence, for each pound of steam condensed, it will require 1021.6/50 = 20.43 pounds of water. This is called the ratio of injection.

*Vacuum Pump.* — Vapors under vacuum always contain a small proportion of air or non-condensable gases, and in order to maintain the condenser in operation, it is necessary continually

[1] See chapter on Flow of Heat, p. 51.

to remove these gases; otherwise, the vapors to condense could not come into contact with the cooling surface of the surface condenser or with the water in the jet condenser. This is the function of the vacuum pump, which is nothing more than an air compressor operating on the difference between the vacuum and the atmosphere.

With jet condensers, the cooling water entering always has in solution a certain percentage of air, which is liberated in the condenser owing to increased temperature and reduced pressure. It is evident that the required air displacement of vacuum pumps for jet condensers is necessarily greater than for surface condensers.

*Barometric Condensers.* — Most jet condensers on evaporators are operated "barometric," the water leaving the lower part through a barometric column or pipe which is long enough to overcome the pressure of the atmosphere. This pipe is water sealed in the hot well below, and this permits a free outlet for the injection water as soon as it reaches the bottom of the condenser.

There is being used more and more to-day a type of jet condenser wherein water is admitted through nozzles under slight pressure. The streams from these nozzles converge into the barometric outlet at the bottom, and thus produce an ejector effect which entrains all of the non-condensable gases, discharging them into the hot well below with the accompanying hot water. The pressure required is not very great, and the consumption of water is as economical as any standard condenser operating under similar conditions. It has found recently many extensive applications with evaporating apparatus on account of its simplicity and ease of operation (Fig. 28).

**Heaters.** — As outlined in other topics of this discussion, Rillieux's Second Principle had particular reference to the economical heating of solutions. This text would therefore be incomplete without some discussion of the apparatus used to do the actual heating.

Heaters and surface condensers are closely related. In condensers, it is usually the case that a large quantity of water is heated through a small range of temperature, whereas with heaters, it is a small quantity of solution raised through a high range.

*Steam Flow.* — As far as the steam side is concerned, it is

PRESSURE
GAUGE

STEAM INLET

WATER
INLET

STEAM
CHAMBER

DRAIN→

VACUUM
BREAKER

←TAIL
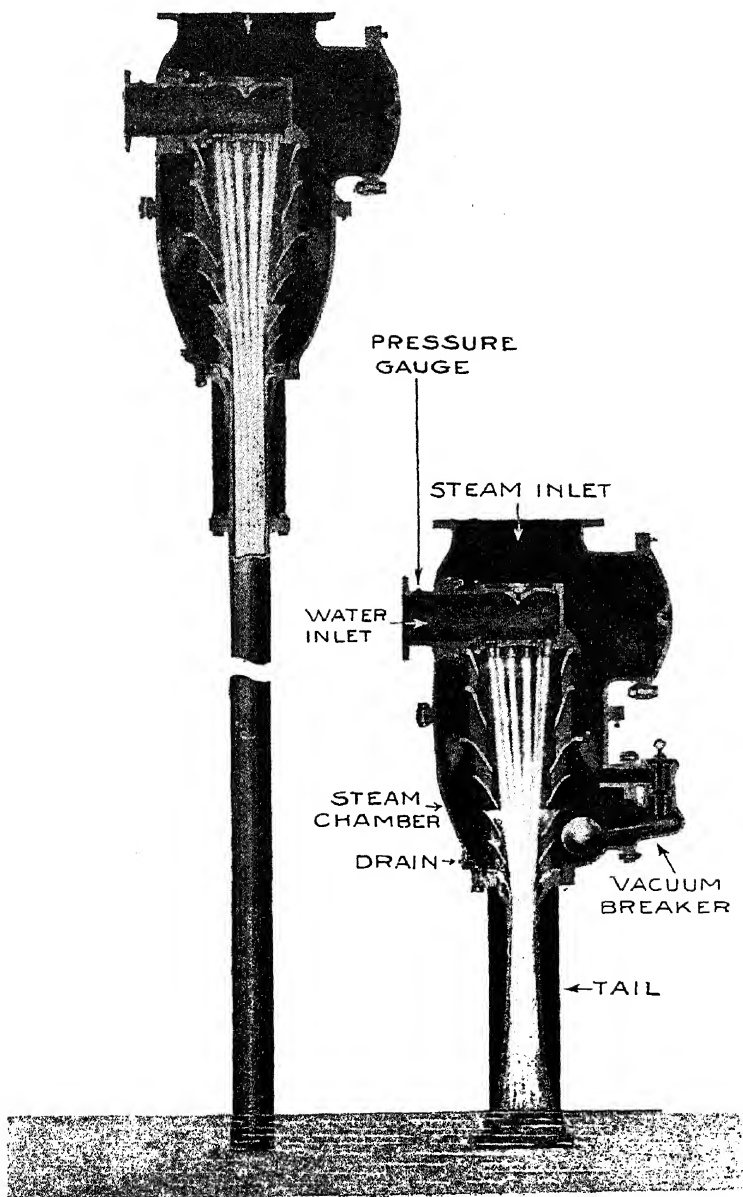
FIG. 28. Ejector Condenser.

advisable so to arrange the design by proper baffling or other means that steam progresses forward through a predetermined path, and it is preferable that the cross-section of the path be very materially reduced towards the end in order to keep the steam or vapor moving fast. This has the further advantage of driving all the non-condensable gases to one point for removal. Preferably, the path of steam should be from the top of the heater in a generally downward direction, while the juices being heated are progressing upward; in other words, counter current. This can best be provided in a horizontal heater, and is doubly important when operating on vapors under a partial vacuum (Fig. 29).
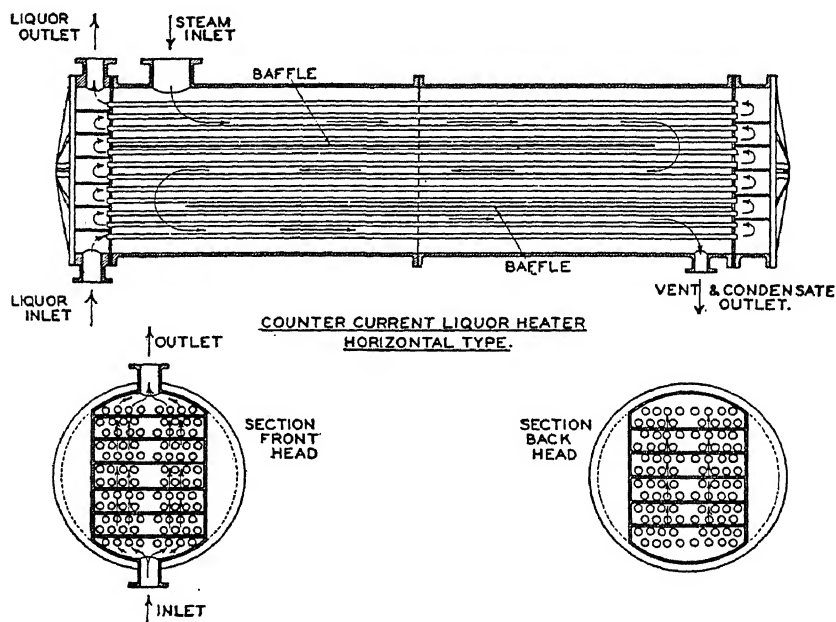


FIG. 29.   Counter Current Liquor Heater, Horizontal Type.

*Liquor Flow.* — As regards the liquor side of the tubes, it is now almost universal practice to arrange the heads of heaters with cells or compartments compelling the flow to take place through a limited number of tubes at a time in order to maintain a high velocity. It will be noted from the accompanying graph

(Fig. 30) what an important influence velocity of liquid travel has upon heat transmission. Not only this, but most solutions being heated form incrustations upon the surfaces, and by
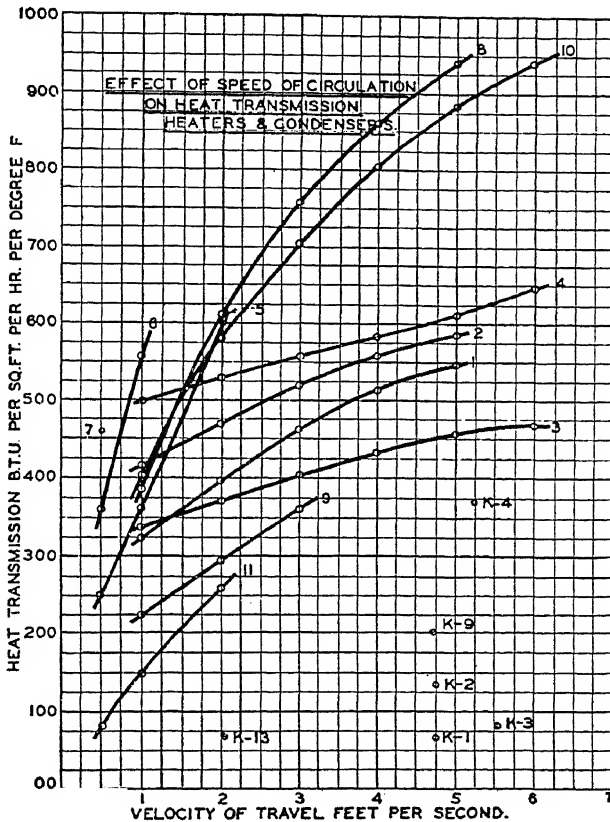


FIG. 30. Effect of Speed of Circulation on Heat Transmission in Heaters and Condensers.

maintaining high velocities, these are greatly minimized. Good practice for liquor heaters require velocities of from five to eight feet per second. Such operation involves serious friction losses which must be borne as part of the cost. Many of our heaters are designed for 100 lbs. pressure on the juice side to take care of this friction loss, for very often, three or four heaters may be operated in series with one pumping. As an example, one sugar

factory uses four heaters in series, the first being a heat exchanger between condensate from an evaporator and cold juice; the second, a stage of vapor heating; the third a heater using flash at 212° from another process; and the fourth, a heater on exhaust steam.

*Heat Transmission.* — In estimating the transmission of heat obtainable commercially, smaller ratings are used than in surface condensers, in the neighborhood of 250 B.t.u.    In calculating the temperature differences, the logarithmic mean of the ingoing and outgoing juice temperatures must be taken for one side, and steam or vapor temperature for the other.[2]    Excessive heating surface is not a fault, as it permits smaller terminal differences, and therefore more efficient vapor heating.

*Temperature Control.* — With ample heating surfaces, it is possible to arrange a very satisfactory temperature control by floating on a given steam pressure whose temperature is what is required, assuming a 0 terminal difference.    Charts from recording thermometers sometimes look like circles drawn with a compass with this method of control.    Extra heaters must always be provided, as they have to be cleaned very often to maintain efficiency.

*Coil Heater.* — Another type of heater which has given very good results is the so-called "coil heater."    This design consists of a solenoid coil installed in a cylindrical chamber, with liquid being pumped through the inside of the coil at a very rapid rate. In fact, the rate of liquor flow is so fast that the heater does not require cleaning.    The velocities range from ten to fifteen feet per second or more.

Single pass heaters, i.e., heaters without restricted juice cells wherein the juice passes through the tubes only once should never be used.    They are very cheap per square foot of heating surface, but have an extremely low coefficient of heat transmission on account of their inherent slow velocity.    They are subject to bad stream lining, wherein the film of juice next to the metal of the tube is heated, leaving the core unaffected or partially heated. They foul very rapidly, have large terminal differences, and are very large for the work required.    They are certainly poor for vapor heating.

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[2] See chapter on Flow of Heat, p. 48.

**Batch Operation.** — In a few specific cases, it becomes necessary to operate discontinuously in batches, feeding the solution into the evaporator as vaporization takes place, concentration increasing progressively to the end, winding up with a batch which is discharged, and the operation resumed as before. Here, the concentration changes during the batch, and generally the volume also. The B.P.R., the hydrostatic head, the viscosity, the concentration, and the rate of evaporation all change.

An outstanding example of this is the ordinary vacuum pan used in the sugar industry. The general arrangement is shown in the accompanying illustration (Fig. 31). In this design, the surface is made up of two parts, a small coil in the conical bottom using live steam, and a "calandria," or steam belt, using exhaust steam. Modern practice has now eliminated the coil entirely, all the work being done by the calandria, which is provided with tubes 4″ or 5″ diameter by about 48″ long, and a large central downtake or circulating tube.



CALANDRIA VACUUM PAN FOR SUGAR WORK.

STEAM

FIG. 31. Calandria Vacuum Pan for Sugar Work.

In running this pan, the work is different according to the stages of syrup exhaustion. In raw sugar factories, three types of batches or "strikes" are usually made, identified as "A," "B," "C." After normal operation in the sugar factory is established, the cycle is about as follows:
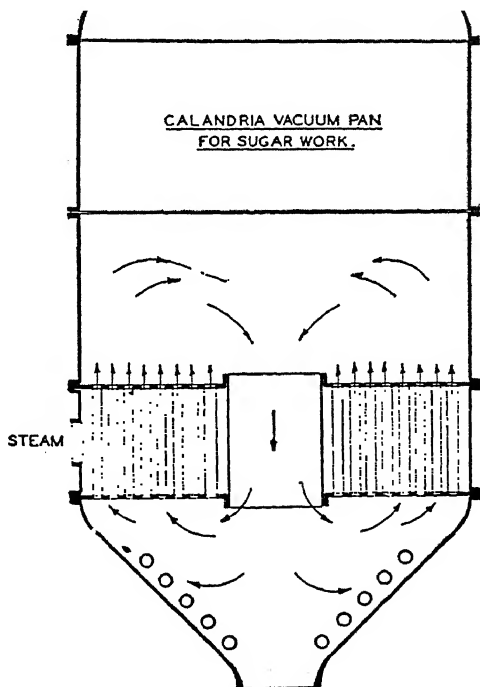
1. Concentrated syrup from the multiple effects is drawn into

the pan at a density of 60 per cent solids, covering the heating surface, after which steam is turned on, and the strike concentrated to about 25 per cent supersaturation under perhaps 25″ vacuum. Then, the temperature is suddenly dropped by raising the vacuum, which results in the formation of an enormous quantity of very fine sugar crystals. After this, "B" molasses is gradually fed in at a concentration of 60 per cent solids, care being taken to feed just fast enough to allow the growth of the crystals without the formation of new ones. This sounds very easy, but is very difficult, and requires great skill. The volume gradually increases until the level is about seven feet above the upper tube sheet, when feed is shut off, and the concentration brought up to about 95 per cent solids. During the "running up" period, the concentration is probably 90 to 92 per cent. This strike is now discharged into so-called crystallizers, where it is kept in motion and continuously cooled slowly for about 72 hours, after which it is sent to centrifugals and purged. The run off is "C," or final molasses, this having been a "C" strike. The sugar called "C" sugar, is now mingled with syrup at 60 per cent concentration, and this mixture is called "magma," and is used as a footing or starting point for "A" and "B" strikes.

2. The "A" strike is made by drawing into the pan sufficient magma approximately to cover the heating surface. Steam is now turned on, and the pan is fed with syrup at a density of 60 per cent to make up the strike as before. Towards the end, the syrup is shut off, and some of the "A" molasses from a previous strike is fed in, to keep down the purity at the fixed standard of 80 per cent. This is called "boiling back." The concentration is now raised to about 93 per cent solids from its original 90 per cent, and the strike is dropped directly to the centrifugals for purging. The sugar is commercial "A" sugar, and the molasses is "A" molasses which will have to be diluted for the "B" strike following to 60 per cent solids.

3. The "B" strike is started with magma as in the previous strike, but is run up on "A" molasses exclusively. The sugar is "B" sugar, and goes out as a commercial product mixed with the "A" sugar. The strike is discharged directly to the centrifugals. The run off "B" molasses is diluted to 60 per cent solids, and all goes to the "C" strike described first. The purity of the strike is 70 per cent. The final concentration is at 94 per cent solids.

In the operation of vacuum pans, the effect of viscosity is very

apparent. This viscosity is greater with the low grade strikes, and as a consequence, they take much longer for the same amount of evaporation. The purities of "A," "B," and "C" strikes are 80, 70, and 60 respectively, and with the same pan, the time required for the strike is two hours, four hours and eight hours, respectively.

*Hydrostatic Head.* — The effect of the so-called hydrostatic head is also very much in evidence. The evaporation at the beginning of the strike is at least three times as fast as at the end. Extensive tests have shown that heat is transmitted mostly as a heating operation, and not direct evaporation. This latter takes place by flashing at the boiling surface. It has also been proven beyond dispute that circulation is extremely sluggish at the end, being a matter of a fraction of an inch per second, and not feet. The coefficient of heat transmission varies from perhaps 250 down to less than 5. It is therefore evident that it is very difficult to give any accurate transmission data which are all warped by local variable conditions, and reliance can be placed upon practice alone.

**A Few Details.** — Below are given a few remarks in connection with the design and operation of evaporators not specifically brought out before.

*Vapor Velocities.* — The vapor pipes leading from the vapor space of one body of a multiple effect to another, and finally to the condenser, must be proportioned for the work to be done — simply guessing at them will not do. The permissible velocities depend upon the densities of the vapor. Good practice involving reasonably low friction losses calls for 75 to 100 feet per second in exhaust pipes, 100 to 125 feet per second in intermediate vapor pipes, and not over 250 feet per second to the condenser.

*Size of Tubes.* — As regards the size of tubes to be used in evaporators, there is no rigid rule, but it is unwise to deviate from established practice, and the range is pretty well covered between $1\frac{1}{4}''$ and $3''$, depending upon the design. For vertical evaporators, small diameter tubes are used under pressure, and large ones under vacuum on account of the larger specific volume of vapor. If very long tubes are used, expansion must be provided for.

Concerning the steam compartments, ample area must be allowed for the free passage of steam or vapor through the heating

surface. Preferably, it should follow a definite path, driving the non-condensable gases to one point for easy removal; otherwise, parts of the heating surface are sure to become air or gas bound with reduced transmission of heat.

*Condensate Drainage.* — Ample drainage must be provided for the water of condensation. The drain pipes must be large enough to give velocities not exceeding three feet per second. If the evaporator is set high enough, drainage from the vacuum bodies can take place by gravity through a barometric column. In such a case, the pipe should be bottle tight, otherwise, air leakage will absolutely prevent drainage. If the apparatus is too low for this, then it becomes necessary to remove the condensates by a pump especially arranged for this purpose. If the pump is of centrifugal design, a check valve should be placed on the discharge, and an equalizing pipe connected from the eye of the pump to the steam chest being drained.

*Air Vents.* — Each steam compartment must be vented to release the non-condensable gases. If the bodies are under pressure, vent to the atmosphere; if under vacuum, vent to the condenser. Be sure to make the vent header much larger than the sum of the areas of the individual vent pipes, otherwise, the bodies closest to the condenser will not vent.

*Feed Pipes.* — The arrangement of feed pipes should also be studied well. As to size, velocities in excess of four feet per second must not be used. The inlet and outlet of liquor from each body must be such that the solution at the point of highest concentration is removed undiluted with incoming feed at a lower density.

*Gauges.* — The apparatus should be well provided with thermometers, vacuum gauges, pressure gauges, level gauges, peep holes, and other necessary appurtenances. Nothing is more disconcerting than to have to work without sufficient indications.

The apparatus should be well insulated against heat losses by radiation. It pays dividends out of all proportion with the investment.

Quick dumping and systematic cleaning to avoid loss of valuable time should be provided for.

*Vacuum Pumps.* — If vacuum pumps are used, a stop valve should be placed in the suction, and a calibrated orifice on a valved side arm between the valve and the pump, by means of which it can be tested for efficiency of displacement. The pump

should be run full speed with the stop valve shut, and the calibrated orifice open. The vacuum maintained when the pump is new should be noted, and a record made for periodic checking and comparison. As soon as the vacuum shows a material drop, the pump should be repaired, it may need only a renewal of the valves.

Proper operation should be insisted upon. The operators have a tendency to carry the levels too high, because it is easier, and requires less attention. Fouling and loss of capacity are the result. It is essential that the operation be uniform and continuous.
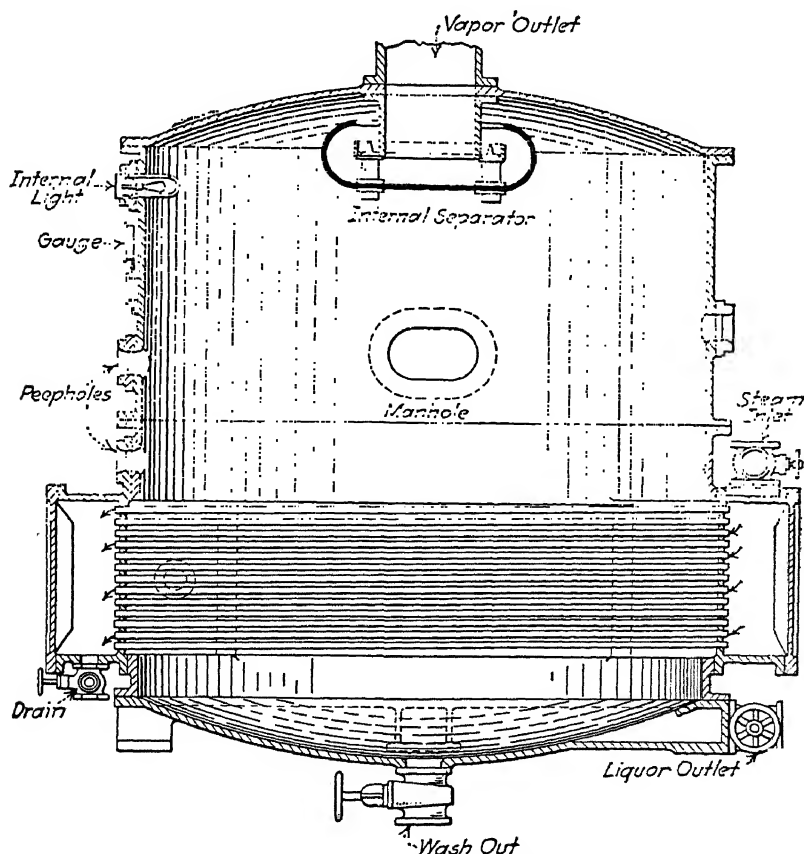


FIG. 32. Zaremba Horizontal Tube Evaporator.
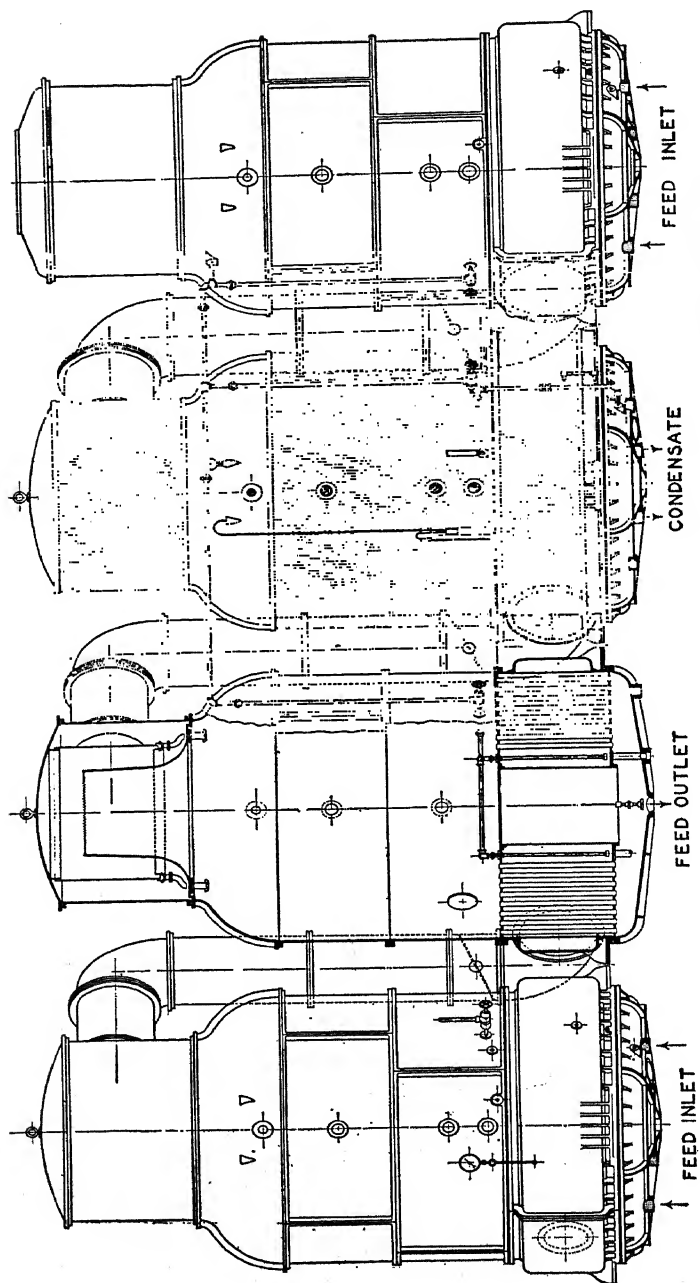
Fig. 33.  Typical Standard Tube Evaporator Showing Bodies Stripped, in Section and Fully Mounted.

**Types of Evaporators.** — Below are given brief descriptions and illustrations of the more common types of evaporators in use in industry.

*The Horizontal Tube Evaporator* shown in illustration (Fig. 32) is a type in very common use in the chemical industries and in beet sugar manufacture. The surfaces are submerged in the solution to be evaporated, and steam is on the inside of the tubes as indicated. The circulation currents are up through the tube bundle, and down on both sides of it in the space between the tubes and the shell. The tubes are packed on both ends with



—The Principle—

—Its Application—
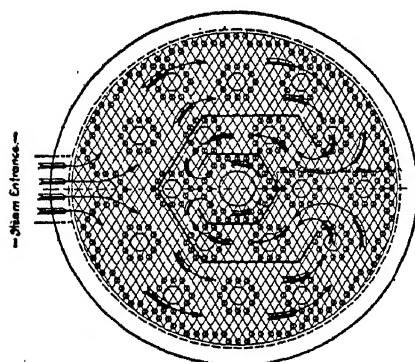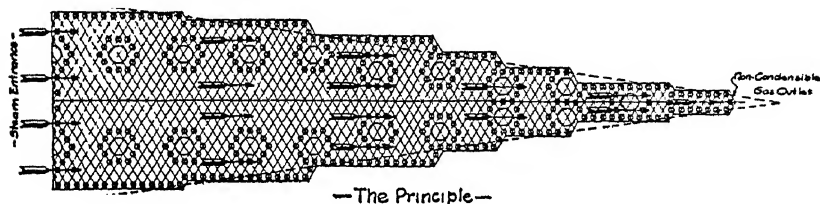
Typical
—Layout of Tube Sheets—
— The Webre Evaporator —

Fig. 34.  Layout of Tube Sheets in Webre Baffled Evaporator.

ferrules, and can be easily removed. They are pitched in the direction of steam flow to ensure proper drainage.

*The Standard Effect*, Fig. 33, has vertical tubes three to six feet long expanded into tube sheets fastened between the main flanges of the body. There is a central downtake or circulating pipe, and sometimes several, for the return of liquids to the bottom for

another pass through the tubes.  This type of evaporator is
sometimes supplied with baffles in the steam space as shown in
Fig. 34, which materially improve the conditions for efficient heat
transmission on the vapor condensing side.  Standard Effects are
used in large numbers in the sugar industry, as well as many
others.
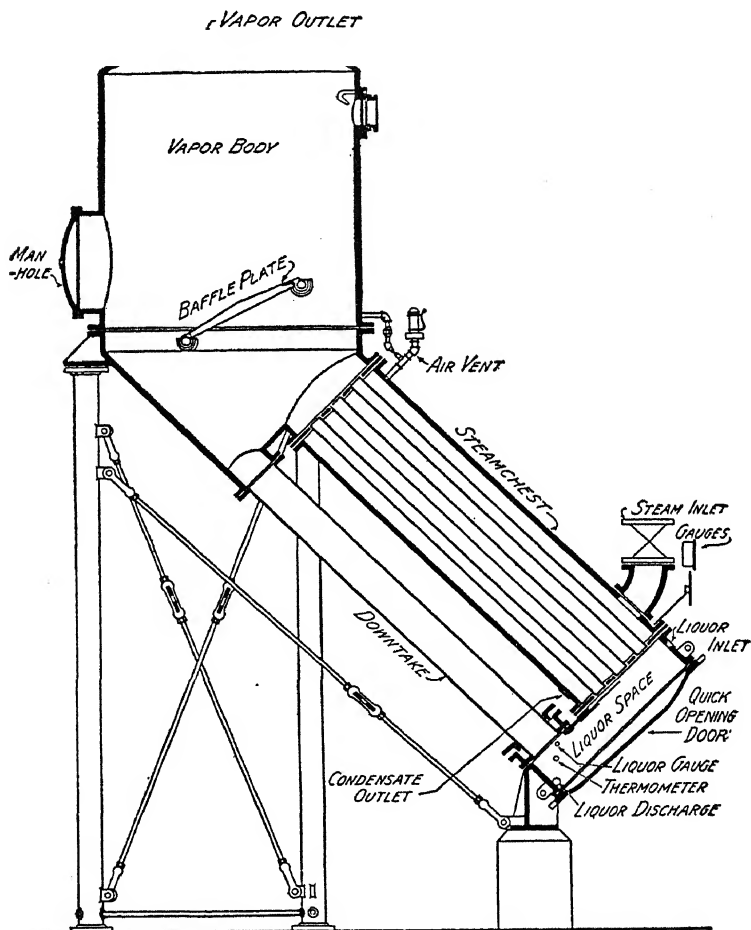


Fig. 35.  Inclined Tube Evaporator.

*The Inclined Tube Evaporator* is shown in Fig. 35.   It operates
very well, and has found many applications.   On large sizes, the

tubes in the lower bank suffer excessively from hydrostatic head loss due to the inherent character of the design.

In the *Basket Type Evaporator*, Fig. 36, the heating surface is
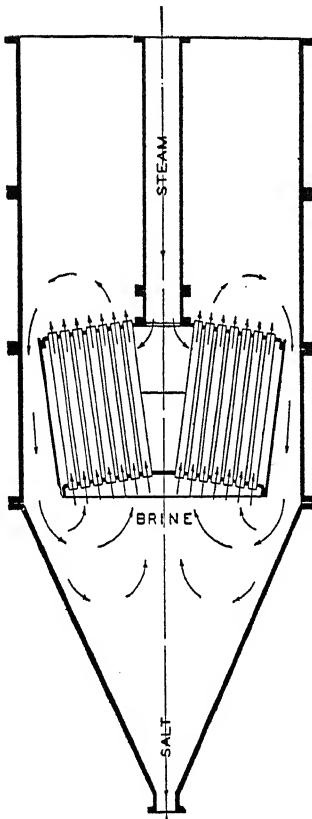


FIG. 36.  Basket Type Salt Evaporator.
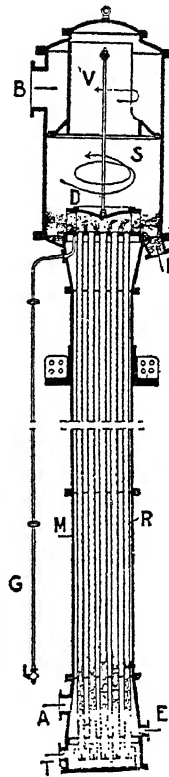


FIG. 37.  Kestner Vertical Single Effect Pressure Evaporator.

installed in a separate drum, which is located inside of the body. Steam enters the center of the drum on top.  Circulation takes place in the annular space between the drum and the shell.  This type has been used very extensively in the past for evaporating caustic soda solutions.

The *Kestner Evaporator*, Fig. 37, is probably the pioneer among the long tube type vertical evaporators.  These tubes are about

24 feet long, and from 2 to 3 inches in diameter. The heat transmission is excellent, but the danger of entrainment very great. That is its weak point. Regulation is tricky. For efficient operation, it is essential that the liquid being evaporated
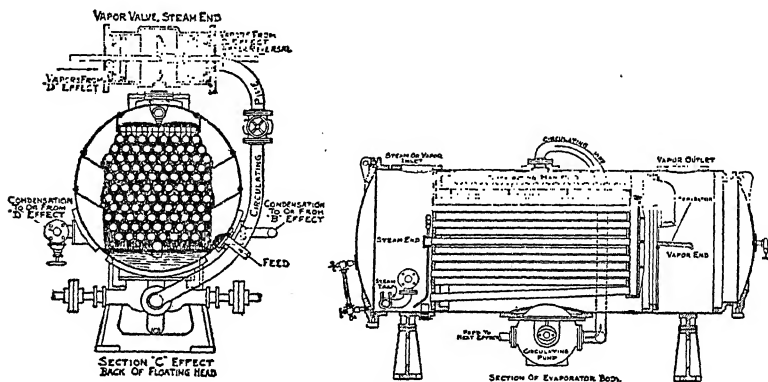


FIG. 38.   Lillie Evaporator.

enter the apparatus at least at the boiling point, otherwise, the velocity at the lower ends of the tubes will be very sluggish. The Kestner is the well known "climbing film" type.

The *Webre Long Tube Evaporator*, Fig. 34, was designed by the author. Its operation is quite similar to that of the Kestner above, except that it is provided with circulation. In the Kestner, the liquid only makes one pass through the tubes and leaves. Extraordinary precautions have been taken against entrainment loss, and as a consequence, this inherent type defect has been obviated. The feeding system also has been modified so that proper control is reliable and easy.

The *Lillie Evaporator*, Fig. 38, is the original film evaporator with mechanical circulation. A pump is provided in the lower part circulating the liquid and spraying it on the heating surface. Steam enters one end of the tubes, water draining backwards against the flow of steam or vapor. The other end of the tubes is blanked off and provided with a small orifice for the release of non-condensable gases. The liquor in the circuit is very small in amount, and thus remains in the evaporator a very short period of time, an important factor in evaporating delicate solutions. When used as a multiple effect, it is provided with two con-

densers, and by means of an ingenious system of special valves in the vapor pipes, the evaporator can be reversed very quickly. In this event, the order of the individual effects is changed, the first effect becoming the fourth.

The *Manistee Evaporator* usually built in very large sizes, Fig. 39, finds an extensive application in the large scale evaporation
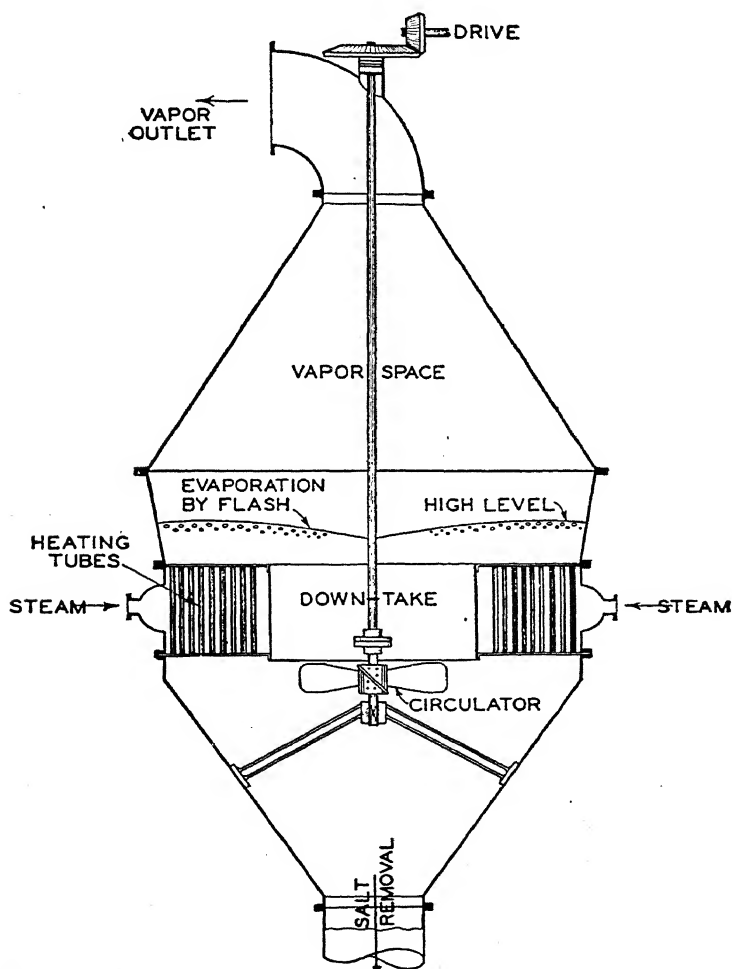


FIG. 39. Section of Manistee Evaporator with Mechanical Circulation.

of salt brines. It has mechanical circulation provided in the central downtake, consisting of a propeller which pushes the brine through the tubes. This evaporator is also characterized by its peculiar arrangement of quadruple vapor pipes.

Among the more recent successful evaporators is the *Swenson design* by Prof. W. L. Badger. This apparatus is provided with intensive mechanical circulation, the liquor being forced through

ENLARGED TUBE SECTION

TYPICAL COIL.

DETAILS OF HEATING SURFACE
REILLY MULTICOIL EVAPORATOR
SELF-SCALING.
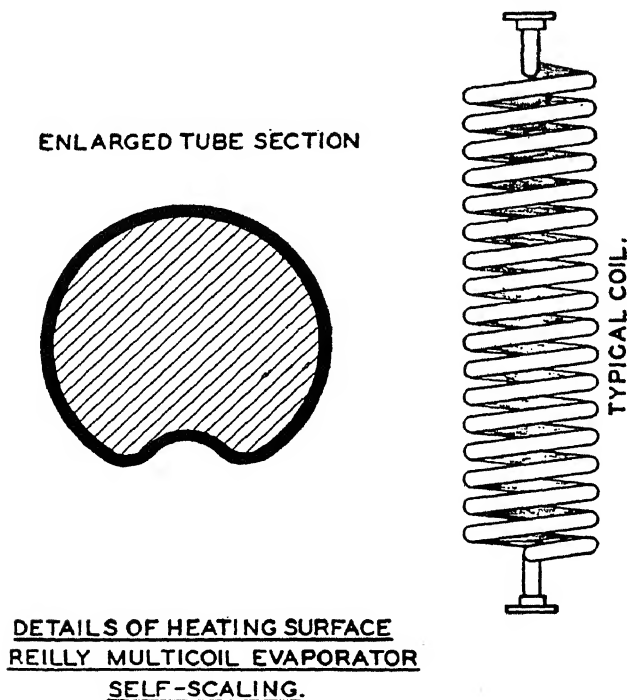
Fig. 40. Details of Heating Surface Reilly Multicoil Evaporator Self-scaling.

the tubes of the heating element by a centrifugal pump. As it leaves the upper ends of these, it is deflected by a circular baffle into a thin sheet which impinges upon the walls of the evaporator. There is practically no trouble from accumulation of salt or scale in the tubes due to the high velocity. The vapor liberating area is very great, and therefore, the B.P.R. should remain close to the theoretical. This design has recently found extensive successful application in the evaporating of caustic soda solutions.

*Distilled Water.* — For the production of distilled water makeup

for steam boilers, a type of evaporator is shown in Fig. 40, wherein steam is condensed in coils of an odd section so interwoven that they will be subject to material physical deflections with variations of temperature and pressure.   These changes of shape cause the release of accumulated scale on the surfaces, and thus permit sustained heat transmission at a fair rate.   Besides this particular design, there are quite a number of other types all depending upon the principle of surface deformation for continuous scale removal and reasonably regular good transmission of heat.   In all cases, the water fed to the evaporator is unfit for boiler feed as it contains a large proportion of scale forming salts in solution usually compounds of calcium and magnesium.   In ordinary evaporators this would result in very rapid lowering of the rate of evaporation, and loss of capacity.

<div align="center">PROBLEMS</div>

10. Hot condensed steam at 212° F. is taken from the steam coils of one effect into those of the next effect where the pressure is 12 inches of mercury absolute. What per cent of the water will flash into steam?

11. Sucrose solutions in water follow Raoult's law up to a concentration of 50 per cent by weight.   Calculate the boiling temperature of the following solutions under the conditions stated:

(*a*) 40 per cent solution at 760 mm. pressure.

(*b*) 40 per cent solution, 4 feet below the surface of the liquid if the surface is at 760 mm. and the specific gravity of the solution is 1.18.

(*c*) 40 per cent solution, 4 feet below the surface, if the surface pressure is 2 inches of mercury absolute.

(*d*) 50 per cent solution, 4 feet below the surface, if the surface is at a pressure of 2 inches of mercury absolute.

12. (*a*) A double effect film type evaporator is to be designed to handle per hour, 1000 pounds of a dilute, aqueous solution of a colloidal material which has substantially no effect on the boiling point of the solution, evaporating 900 pounds of water per hour.   Steam is available at 212° F. for use in the first body and a vacuum of 28 inches of mercury, normal barometer, may be expected in the vapor space of the second.   The over all coefficient of heat transfer may be taken to be 400 and 200 in the first and second bodies respectively and the areas of the heating surface in the two bodies are to be the same.   Assuming as a first approximation that there will be equal evaporation in each body, calculate the temperature and pressure in the vapor space of the first body.

(*b*) Using the temperature obtained in problem 3(*a*) for parallel flow, and calling the specific heat of the solution = 1, set up a heat balance for the first body, calling the amount of steam *x*, the evaporation *y*, if the feed enters at the boiling temperature of the first body, using the latent heats for the proper temperatures.

(*c*) The condensed steam is taken from the steam coils of the first body into those of the second.   Calculate the B.t.u. per hour that will be obtained as flash of the condensate, in terms of *x*.

(*d*) Calculate the B.t.u. liberated by self-evaporation of the superheated solution in the second body, in terms of *x*.

(*e*) Set up a heat balance in the second body, eliminating *y* and solving for *x*.

(*f*) Re-check the original assumption of equal evaporation.

(*g*) From the re-checked value of *x*, calculate the heating surface needed.

13. (*a*) Calculate the heat transmission for the four bodies of the Quadruple Effect Evaporator discussed in this chapter, making the proper corrections for hydrostatic head, assuming that the heating surface is submerged under 12″ of liquid, the specific gravities being 1.076, 1.101, 1.150, and 1.290 in the first, second, third, and fourth effects.

(*b*) In the same example, if the condensate were flashed from the steam belt of the second effect to that of the third, and also, from the third to the fourth, how much more evaporation would have taken place, all other conditions remaining the same?

(*c*) Assume that a condenser is attached to this quadruple effect, and that the temperature of injection water is 80° F., the terminal difference being 10° F. What is the amount of water required by the condenser in gallons per minute? What is its efficiency?

(*d*) Following the recommendations suggested in this chapter, what should be the size of steam pipes, vapor pipes, feed pipes, and condensate drains for the same apparatus? (Refer to Steam Tables.)

(*e*) Calculate the volume of vapor released by the juice as it passes from each body to the succeeding one. (Refer to Steam Tables.)

(*f*) How much difference would it make in the steam consumption of this quadruple if the temperature of the incoming juice feed had been 205° instead of 180° F.? How much for 150° F.? Assume that the pressure conditions have remained unchanged.

(*g*) In your opinion, how much loss of capacity would the original quadruple have suffered if the hydrostatic head had been 24″, instead of 12″, which was assumed in that case? Justify your opinion.

(*h*) How much more capacity would the quadruple effect have developed if the steam pressure had been raised to 10 lbs. gauge, and the vacuum increased to 27″?

(*i*) How much less steam would have been required by a quintuple effect operating on the same pressure and final vacuum carrying the same load?

(*j*) Set up a heat balance for the same problem, assuming that vapors will be robbed from the first body of the quadruple for heating juice from 100° F., to 205° F., the quantity being the same, 100,000 lbs. per hour.

(*k*) How much surface would be required in a properly designed heater to operate with the quadruple?

(*l*) If a thermo-compressor were attached to the first body of the quadruple effect, and supplied with steam at 185.3 lbs. gauge, and 150° superheat, how many pounds of vapor would it compress from the vapor space back into the steam space, assuming the efficiency to be 25 per cent? (Use Steam Tables and Mollier Diagram.)

14. An evaporator for the production of distilled water on a large scale is supplied with feed water at 212° F. It is operated by a turbo-compressor having an efficiency of 40 per cent. The surfaces are such that it is possible to operate with 3 lbs. gauge in the steam space, while the vapor space is at atmospheric pressure. Assuming negligible radiation loss, how much power will it take to produce 200 gallons of distilled water per minute? (Use Steam Tables and Mollier Diagram.)

# CHAPTER IV

## PRINCIPLES OF FRACTIONAL DISTILLATION AND THE DESIGN AND USE OF COLUMN STILLS

### THEODORE BAKER, B.Sc.

The process of distillation is similar in many ways to evaporation, the chief difference being that condensation of the vapor is vital to the process because the distillate is the important product for which the process is carried out; while in evaporation the substances in solution are the products whose recovery is sought. The principles governing the process of evaporation have already been discussed insofar as they concern the separation of a volatile from a non-volatile liquid or solid. The apparatus required for distillation must include a kettle or other apparatus in which the liquid is heated and a condenser for condensation of the distillate. If two or more volatile liquids must be separated a fractionating column must be connected between the kettle and the condenser. If the operation is carried out in a vacuum a pump must be added.

The most difficult problem confronting the chemical engineer is that of the separation of two or more volatile liquids or solids. Fractional distillation is one of the important means for making this separation and obtaining substantially pure liquids. Sometimes it is the sole method of separation and purification used and sometimes it is used in combination or sequence with chemical treatment, crystallization or differential solution.

**Vapor Pressures.** — The most important property of a substance as affecting its behavior on distillation is its saturation vapor pressure (also called "vapor tension"), a property which rises continually with rising temperature, and has but one value for a given temperature. An immense mass of data on the vapor pressures of various solid and liquid substances has been collected and may be found tabulated in standard reference works.[1] If

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[1] Such as "International Critical Tables, Vol. III," the "Physical Chemical Tables of Castel Evans, Vol. I," and Rechenberg's "Einfache und Fraktionierte Destillation."
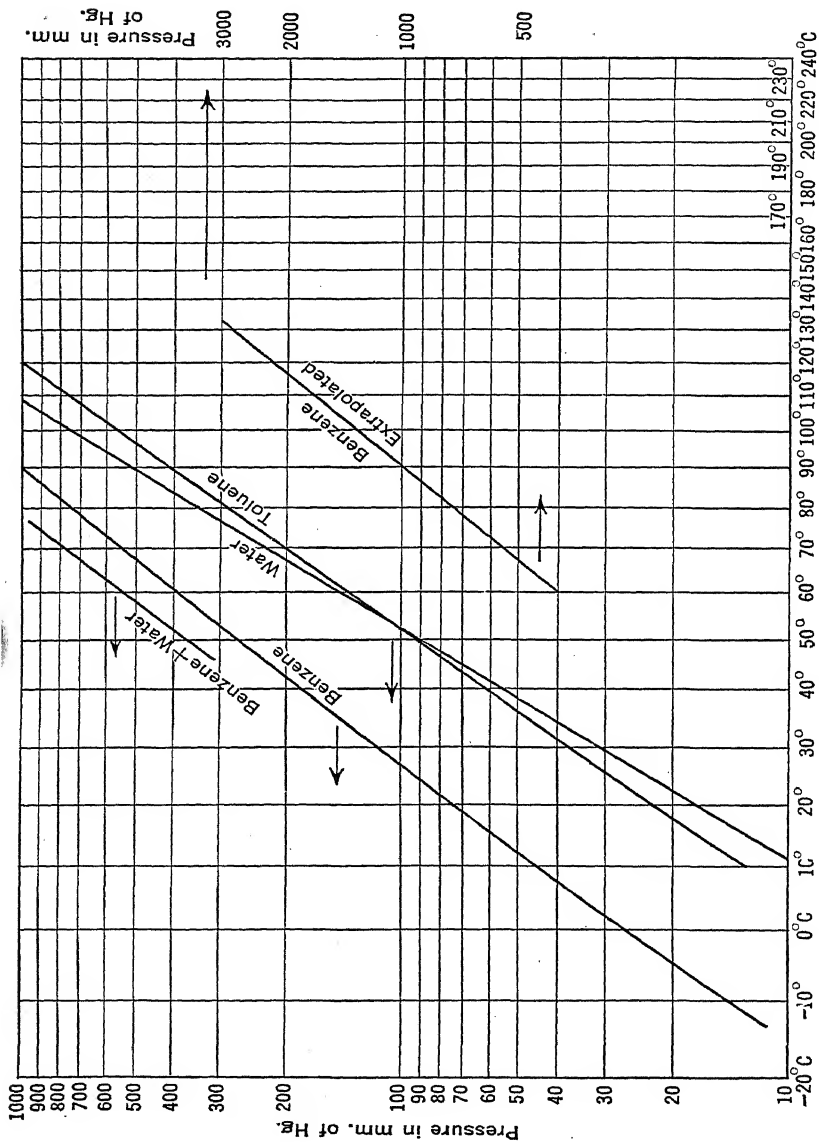
Fig. 41. Vapor Pressure Curves.

the data for any selected substance are plotted on common section paper with temperature taken along the abscissae and pressures along the ordinates a curve drawn through the various points will be found of an inconvenient form and hard to interpolate or to read with any degree of accuracy.   A more convenient form of graduation for plotting these curves is one in which the ordinates are taken proportional to the logarithms of the pressures and the abscissae are measured on a scale proportional to the inverse of the absolute temperature, that is $1/t^\circ$ C.$+273.1$.[2] Some sample curves plotted on a sheet of paper thus graduated are shown in Fig. 41.   It will be seen that the curves closely approximate straight lines and may be used both to interpolate and extrapolate available data with very fair accuracy.   They cannot, however, be so used continuously to below the melting point, nor beyond the "critical temperature," that is, the upper limiting temperature beyond which there is no separation of liquid from vapor, but only one dense vapor phase is possible.

Sometimes vapor pressure data are desired for substances not given in the tables in detail, but for which only a single point is available (generally the boiling point under 760 mm. pressure).   The following rule, due to Ramsay and Young, is then of service:

*For nearly related substances the ratio of the absolute temperatures at which they have the same vapor pressure is constant.*

Thus, taking data for benzene and toluene as examples, we have:

| Saturation Pressure in mm. Hg | Corresponding Temp. °C. | | Absolute Temperatures | | Ratio of Absolute Temperatures $\frac{Toluene}{Benzene}$ |
|---|---|---|---|---|---|
| | Benzene | Toluene | Benzene | Toluene | |
| 700 | 78.5° | 108 | 351.6 | 381.1 | 1.084 |
| 500 | 68° | 97 | 341.1 | 370.1 | 1.085 |
| 300 | 53° | 81 | 326.1 | 354.1 | 1.085 |
| 200 | 42.5° | 69.5 | 315.6 | 342.1 | 1.085 |
| 100 | 26.7° | 52 | 299.7 | 325.1 | 1.085 |

Such examples can be multiplied *ad libitum* if the pairs are chosen in the same chemical class and not too dissimilar in structure or

[2] Paper with this graduation is supplied by the Educational Exhibition Co. of Providence, R. I., style 4442 special.

composition.    It is obvious that the constant ratio can be calculated from the temperatures for any one pressure, and from this the corresponding temperatures for the substance for which data are deficient.

**Mixtures Containing Undissolved Ingredients.** — Before subjecting a mixture to distillation it is generally desirable to make such mechanical separation as may be practicable, of matter not actually in solution in the bulk of the material.    This is still advisable even when there is a separation into two layers, both layers containing both ingredients in differing proportions. When the undissolved matter is a solid it may generally be filtered out, but when there are two mutually insoluble liquids it is nearly always better to allow them to settle (warming if necessary) and to decant the lighter layer from the surface, while the heavier is run off from below.    The reason for this practice is that when two mutually insoluble liquids are boiled together, as for example benzene and water, they distill over together in a fixed ratio as long as two layers remain.    The pressure under which the mixture distills is the sum of the vapor pressures of each insoluble layer considered separately, so that if the external pressure under which they are boiling is one atmosphere, the mixture will boil at such a temperature that the sum of the vapor pressures of the two ingredients is equal to 760 mm. while the amount of each going over is proportional to the product of its molecular weight into its vapor pressure.    In the example being considered the data for the three temperatures 60° C., 70° C., and 80° C. are:

| $T°$ C. | Vapor Pressures | | Total Pressure | Molecular Weights | | Product Mol. Wt. by Vapor Press. | | Per Cent by Wt. in Distillate | |
|---|---|---|---|---|---|---|---|---|---|
| | Benzene | Water | | Benzene | Water | Benzene | Water | Benzene | Water |
| 60 | 388 | 148.9 | 536.9 | 78 | 18 | 30,230 | 2,680 | 91.85 | 8.15 |
| 70 | 542 | 233.3 | 775.3 | 78 | 18 | 42,250 | 4,200 | 90.94 | 9.06 |
| 80 | 748 | 354.9 | 1,102.9 | 78 | 18 | 58,350 | 6,400 | 90.12 | 9.88 |

To find the temperature at which the mixture boils at 760 mm. pressure, the procedure is thus:

At 70° C. the mixture will boil under 775.3 mm. pressure and

by interpolating either graphically or by calculation we find the pressure drops per 1° C., 17.6 mm. for benzene and 10 mm. for water, or a total of 27.6 mm.   Subtracting 760 mm. from 775.3 mm. gives 15.3 mm. excess pressure, and 15.3/27.6 equals 0.55, indicating that the mixture under 760 mm. should boil at 70° − 0.55° C. or at 69.45° C.

The proportions in which they distill together at this temperature are figured thus:

542 mm. — (17.6 mm. × .55) = 532.2 mm.   Vapor pressure of benzene.

232 mm. — (10 mm. × .55) = 227.8 mm.   Vapor pr water.

| mm. | Mole. Wt. | Product | Per Cent by Weight |
|---|---|---|---|
| 532.2 × | 78 = | 41,520 | 91 Benzene |
| 227.8 × | 18 = | 4,102 | 9 Water |
| | | 45,622 | 100 |

As this accompanying water must be evaporated in addition to the benzene and has a high heat of vaporization compared with the latter, distilling with water is in general more wasteful of heat than distilling dry, especially with substances of low vapor pressure, as then the proportion of steam required is much greater than with a highly volatile oil, such as benzene. Furthermore, the water must be separated afterwards and the oil layer then is in a slightly wet condition, which is generally undesirable.   In spite of these considerations the method is used with advantage under certain conditions as in dealing with emulsions that refuse to "break"; also in distilling volatile oils that occur dispersed in organic matter, such as turpentine and the essential oils, and finally to aid in distilling over material such as stearic acid that would be injured by excessive dry heat (see "Steam Distillation," Chapter V).

Although the above method of calculation is only strictly applicable for such ingredients as are substantially insoluble in one another, it gives fair approximations in cases where the solubility is partial, as long as two layers are present.   A good example is a mixture of iso-butyl alcohol and water which forms two layers boiling together at 90° C. and giving a distillate containing 66.8 per cent by weight of the alcohol, while calculation

would indicate 74.9 per cent alcohol if the above rule prevailed. Similarly, iso-amyl alcohol distills over with water at 96° C. and at 55 per cent concentration, instead of 59 per cent as calculated. In these cases the expulsion of the small residue of water dissolved in the oil when two layers are no longer present is easy and rapid and the same is true of the expulsion of the small amount of the oily body dissolved in the water. Both operations are accompanied by a rapid rise in the boiling point to that of the pure ingredient as the accompanying substance is exhausted.

**Completely Soluble Mixtures.** — In the case of a mixture of two compounds that not only dissolve each other in all proportions, but are also so closely similar in their properties that the mutual attraction of like and unlike molecules in the mixture is nearly the same, the vapor pressure rule is quite different to that given above, but also admits of quite simple formulation, in these terms, . . . "For any given temperature the partial pressure of each constituent is the same fraction of its normal vapor pressure that its molar fraction is of the whole mixture. . . ."

The meaning and mode of application of this rule is best shown by an example, for which mixtures of benzene and toluene may be taken as suitable. We take a series of temperatures ranging from one corresponding to pure benzene (80.2° C. for 760 mm. pressure) to another corresponding to pure toluene (110.4° C. for 760 mm. pressure). Suppose the selected intermediate temperatures are 90° and 100°. In the tabulation (given below) the temperatures are in the first column and the corresponding vapor pressures for benzene and toluene (at saturation) in columns 2 and 3. In Columns 4 and 5 "$M$" represents the number of mols of benzene in 100 mols of the liquid mixture and $(100 - M)$ the corresponding molar per cent of toluene. Then the total pressure of benzene at 90° C. being 1013 mm., its partial pressure in the mixture becomes 1013 mm. $\times M/100$ and the corresponding partial pressure of toluene is 404.6 mm. $\times (100 - M)/100$. Adding these together and equating to the total pressure (760 mm.), we get

$$\left(1013 \times \frac{M}{100}\right) + \left(404.6 \times \frac{100 - M}{100}\right) = 760,$$

$$\frac{M}{100}(1013 - 404.6) = 760 - 404.6 = 355.4.$$

Therefore,

$$\frac{M}{100} = \frac{355.4}{1013 - 404.6} = \frac{355.4}{608.4} = 0.585,$$

or

$$M = 58.5 \text{ mols per cent benzene.}$$

Similarly we may find for 100° C. and 760 mm. $M = 25.5$ while at 110.4° C., $M$ vanishes as the liquid is then all toluene.  The corresponding mol per cent of benzene in the vapor is the same as the percentage that the partial pressure of the benzene is of the total pressure.   Thus for 90° C., the partial pressure = 1013 mm. $\times$ 58.5/100 = 593  mm. and  100 $\times$ 593  mm./760  mm. = 78 molar per cent benzene in vapor.  In the same way for 100° C. at 760 mm., the molar per cent of benzene in the vapor becomes 45.2.

| Temp. 0° C. | Vapor Pressures at Saturation mm. | | Partial Pressures in Mixture mm. Hg | | Molar Per Cents of Benzene | |
|---|---|---|---|---|---|---|
| | Benzene | Toluene | Benzene | Toluene | In Liquid | In Vapor |
| 80.2 | 760 | 293 | 760 | 0 | 100 | 100 |
| 90 | 1,013 | 404.6 | $\dfrac{M\,1013}{100}$ | $\left(\dfrac{100-M}{100}\right) 404.6$ | 58.5 | 78 |
| 100 | 1,344 | 560 | $\dfrac{M\,1344}{100}$ | $\left(\dfrac{100-M}{100}\right) 560$ | 25.5 | 45.2 |
| 110.4 | 1,750 | 760 | 0 | 760 | 0 | 0 |

The molar per cents of toluene are taken by difference or may be calculated independently as a check.   A slide rule is generally accurate enough for these calculations when dealing with practical distillation problems.   While the results obtained as above by calculation, or obtained by direct experiment, may be plotted using the ordinates for temperatures and abscissae for molar per cents as shown in Fig. 42, for practical reasons explained later it is preferable to use the ordinates for molar per cents in the vapor and the abscissae for molar per cents in the liquid, and either to ignore the temperature or note it at intervals along the smooth curve drawn through the plotted points.   See Fig. 43.

Many mixtures are met with in practical work which may be completely soluble in all proportions, but do not obey this simple

law, many of them having a tendency in the direction of the insoluble class. The best known example of this is the mixture of ethanol and water. This mixture when containing 10.6 mol
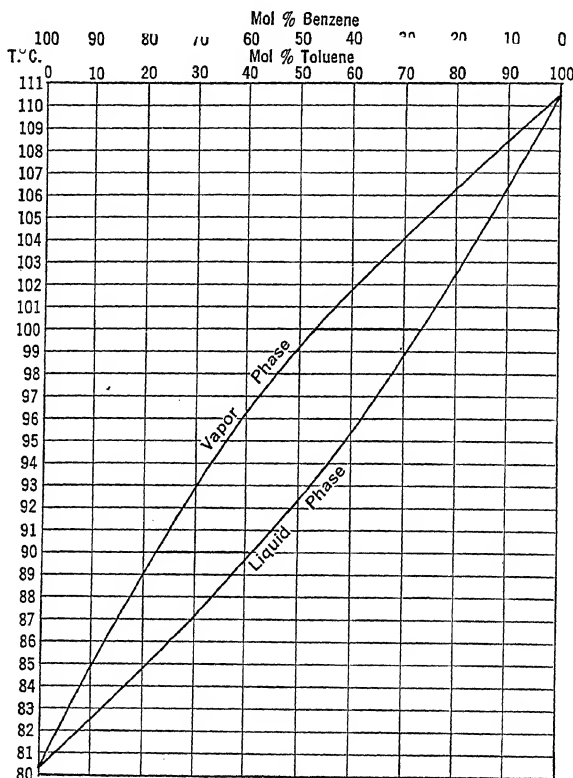


FIG. 42.   Equilibrium Data of Benzene and Toluene Mixtures at 760 Mm. Pressure.

per cent water equal to 4.43 weight per cent, has under 760 mm. pressure a boiling point of 78.15° C. while pure ethanol boils at 78.3° and water at 100° C.

Another class of mixtures, less frequently met with in practice, exhibits a slight tendency for the unlike molecules to combine in an unstable manner. A good example of this behavior is shown by the mixture of nitric acid and water. While pure nitric acid boils at 86° C., a mixture of 68 per cent $HNO_3$ with 32 per cent $H_2O$, both by weight, boils at 120° C., at 760 mm.

**Azeotropism.** — These mixtures of minimum or maximum boiling point are called "azeotropes" and give vapor of the same composition as the boiling liquid and cannot therefore be separated by simple distillation.   A change in the pressure and temperature of distillation alerts the azeotropic composition some-
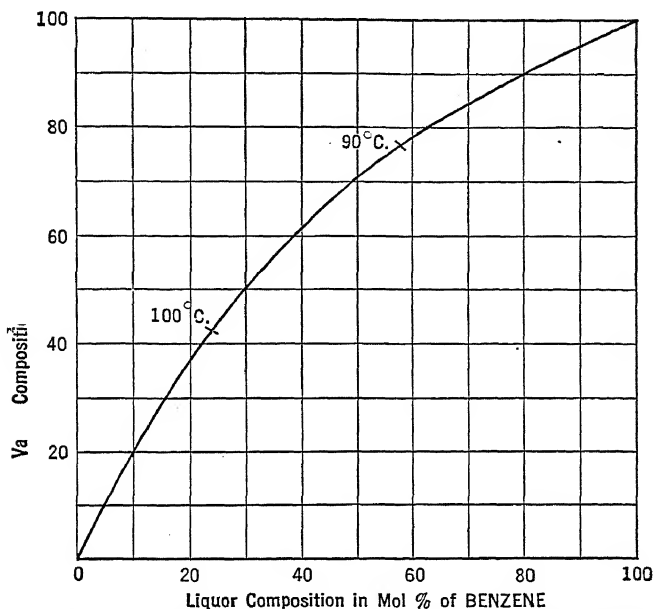


FIG. 43.   Equilibrium Data of Benzene and Toluene Mixtures at 760 Mm. Pressure.

what.   Most frequently such mixtures are dealt with by adding a third component that breaks up the azeotropic mixture.   In this way sulphuric acid added to the nitric acid-water mixture permits strong nitric acid to be distilled off.   For lists of azeotropic mixtures reference may be made to Sydney Young's "Distillation Principles and Processes," p. 49 and especially to the work of Maurice Lecat, "L'Azetropizme," [3] but for a collection of liquor vapor composition curves whether azetropic or not, we recommend reference to "Principles and Practice of Industrial Distillation" by Hausbrand and Tripp.

**Distillation of a Mixture Whose Liquor-Vapor Composition Relations are Known.** — *Reflux.* — To make this subject clear

[3] Henri Lamartin Bruxelles, 1918.

let us take as an example the binary mixture of benzene and toluene whose equilibrium relations, as given roughly in Fig. 43, present no abnormalities. Let us imagine that we have a continuous and constant supply of vapors whose composition is 50 mol per cent each of benzene and toluene and that our aim is to obtain from this a product containing 90 mol per cent of benzene. By reference to Fig. 43 we note that 50 per cent vapor is in equilibrium with 30 per cent liquor. This implies that if the 50 per cent vapor is partly condensed and the condensate returned with the most efficient intimate contact imaginable with the rising vapors the final run-back liquor which is known as reflux, must contain at least 30 per cent benzene. This is the concept of minimum reflux. Its relative amount is figured thus: In some period of time, say an hour, let $V$ represent the mols of vapor entering the apparatus effecting the separation (called a still), let $P$ be the corresponding mols of 90 per cent product taken off and $R$ the mols of 30 per cent reflux returned in equilibrium, then $V = P + R$ for the total mols entering and leaving, and $50\ V = 30\ R + 90\ P$ for the mols of benzene only entering and leaving, i.e., since $P = V - R$, $50\ V = 30\ R + 90\ V - 90\ R$ whence $R(90 - 30) = V(90 - 50)$ or $R/V = 2/3$. This means that at the very least to attain the product desired from the vapor supplied at least 2/3 of the amount of the latter must be returned as reflux, no matter how efficient the still may be. This gives us a clear idea of the necessity of a proper amount of reflux depending on the circumstances when the product is to be more concentrated in low boiler than the vapor supplied.

*Fractionating Column.* — Although such ideal efficiency is unattainable in practical apparatus, we can reasonably expect to attain a ratio about ten per cent higher, or say 74% in the above example. Several varieties of apparatus are used in stills to enable them to approach as nearly as practicable to the theoretical minimum of reflux. The general scheme of them is to have a (partial or complete) condenser which produces the necessary reflux and returns it down a device called "a fractionating column" in which it meets the entering vapors rising from the bottom. In the column an intimate mixing of the rising vapors with the descending reflux takes place with a mutual interchange of constituents, the reflux giving up part of its low boiling constituent (benzene) in exchange for a like number of mols of its high boiling constituent (toluene), until its final composition,

when it reaches the base of the column is so nearly in equilibrium with the entering vapors as not to be practically serviceable for their further enrichment, while the vapors reaching the top are expected to have attained the goal set is the example of 90 per cent concentration.   The simplest way of considering the internal behavior of such a distilling column is to imagine it as being composed of a number of ideal sections placed one above the other and operating in such a manner that the vapor leaving the top of a given section has a composition that is in equilibrium with the reflux leaving the bottom of that section.   Mr. W. A. Peters, Jr., who introduced this concept, called these ideal sections "theoretical plates" and in dealing with columns devoid of plates spoke of the height of an equivalent theoretical plate or briefly an H.E.T.P.

**Thermal Considerations.** — *Trouton's  Ratio.* — At this point it is well to make a digression referring to the heat involved in the problem, which incidentally explains why it is convenient to plot the diagrams in terms of molar concentrations instead of the apparently simpler weight per cent.   There is an empirical rule (commonly called *Trouton's*) having also some theoretical basis, which has been variously stated by different authors, but in its simplest form is written $K = ML/T$ when $M$ is the molecular weight of a substance, $L$ its latent heat of evaporation (calories per gram) and $T$ the boiling point on the absolute scale or 273° plus the boiling point in °C.   $K$ may be called *Trouton's* ratio as it is not a true constant, but while varying only slightly from substance to substance of the same class for a given vapor pressure, as may be seen in Fig. 44, varies quite considerably for one and the same substance when its boiling point is varied by changing the pressure.   From the examples given, and many other like them, it has been found that for the great majority of organic liquids *Trouton's* ratio at atmospheric pressure is around 20.5, and slightly more for substances of higher boiling point.   We can, therefore, state as a consequence that for pairs of substances of the same class where $T$ absolute varies but slightly from one substance to the other, that the molecular latent heat is roughly a constant.   When the variation of $T$ is great there is no serious distillation problem as the separation is easy.

Two important groups of substances call for special mention: the alcohols, including water, and the glycols and glycerine, for

which the *Trouton's* ratio is about 27, and the lower fatty acids, for which no definite molecular weight can be assigned as they gradually dissociate from double molecules to single, with rising



Fig. IV.   Diagram of Values of Troutman's Ratio $K = \frac{ML}{T}$ Plotted against Temperature
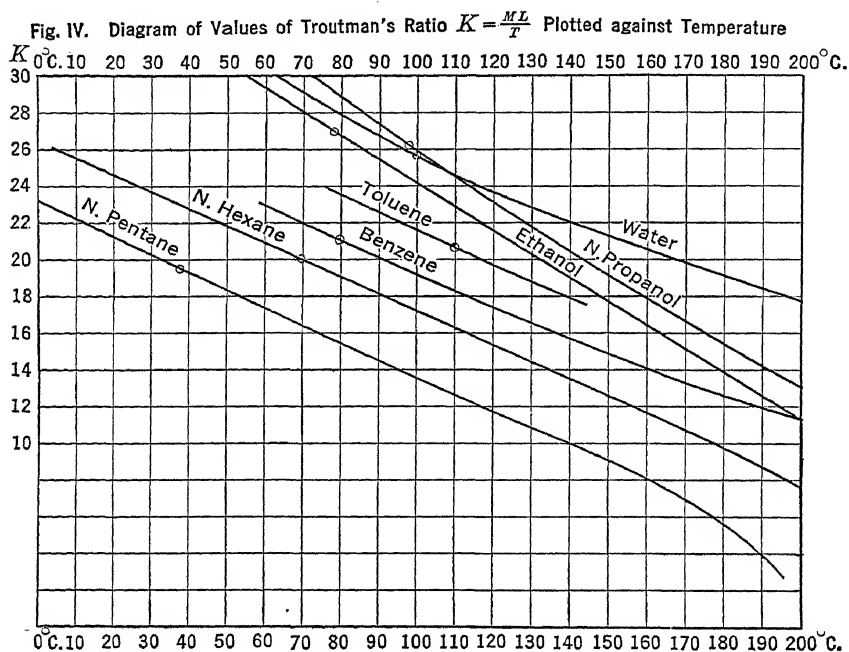
Fig. 44.   Diagram of Values of Troutman's Ratio $K = \dfrac{ML}{T}$ Plotted against Temperature.

temperature.    With these reservations we can state that as a general approximate rule when a mol of one component of a mixture condenses, enough heat is generated to evaporate a mol of another lower boiling component, both, of course, being at the same pressure.    Consequently, since by lagging a fractionating column loss of heat through the walls may be rendered unimportant, in our example each mol of toluene condensing evaporates a mol of benzene and the total number of mols reaching the top of the column is practically the same as the number entering at the bottom in the same time, and the same constancy in number of mols applies to the reflux liquor in spite of the constant changes in the proportions of the ingredients.

*Ideal Column Section.* — We can now return to the consideration of a fractionating column composed of a series of ideal sections, each of which passes upwards a vapor of the concen-

$V_{yp}$

Condenser

$R_{yp}$

$P_{yp}$

$y_b$ = Conc. in $B_z$ of Vapor to Column
$y_l$ =  "    "    "    "    "    leaving Section $l$
$y_n$ =  "    "    "    "    "    leaving Section $n$
$y_p$ =  "    "    "    "    "    to Condenser
$V$ = Mols. Vapor per hour from Still to Column
$R$ =  "    "    "    "    replaced through Column
$P$ =  "    "    "    "    removed as Product

$x_l$ = Conc. of Liquor leaving Section $l$
$x_n$ =  "    "    "    "    Section $n$

Section $n+l$

$R_{xn}$
Section $n$

3

$V_{y2}$  2    $R_{x3}$

$V_{y1}$  1    $R_{x2}$

$V_{yb}$    $R | x_1$

$$V = R + P$$

$$V_{yn} = P_{yp} + R\,x_{n+l}$$

$$V_{yn} = (V-R)_{yp} + R\,x_{n+l}$$

$$y_n = \left(l - \frac{R}{V}\right)_{yp} + \frac{R}{V}\,x_{n+l}$$
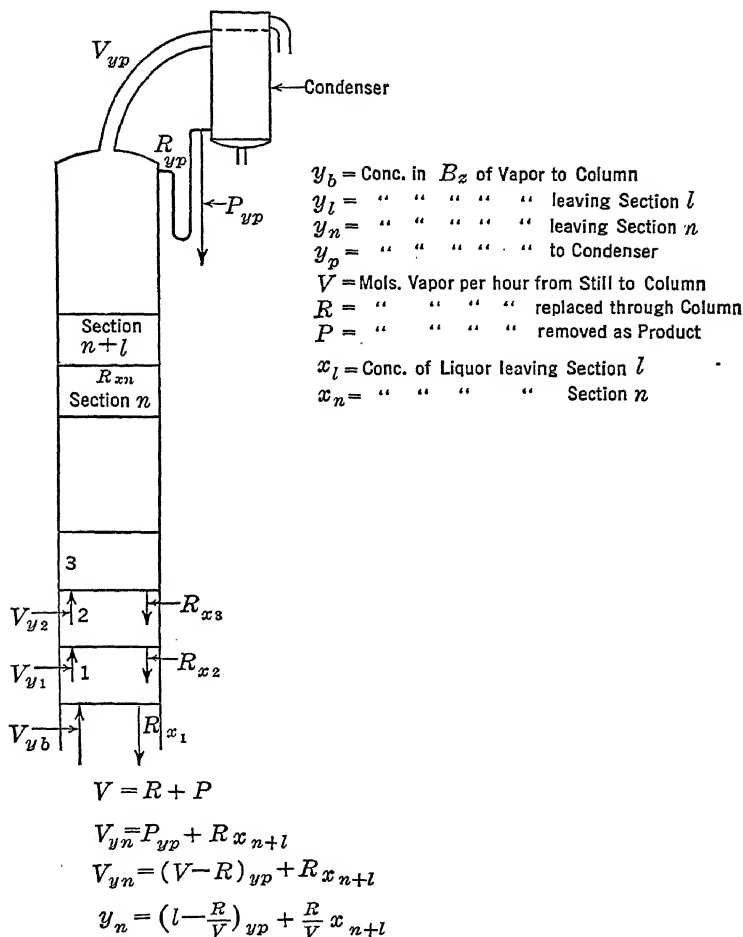
Fig. 45.   Ideal Column Section.

tration which is in equilibrium with the liquor passing down to the next section below.   Let the sketch (Fig. 45) represent such a column whose sections are numbered from the base up.   Then, at any intermediate section numbered $N$, call the molar concentration of benzene in the vapor leaving it $y_n$, and of benzene in

the liquor entering it from above $x_{n+1}$.  Further, call the molar concentration of the product taken off from the top of the column $y_p$ and its amount $P$ mols corresponding to $V$ mols of vapor passing up and $R$ mols of refluxed condensate passing down.  Then equating total mols of benzene rising to the sum of those returned and those in the product we have

$$Vy_n = Rx_{n+1} + Py_p,$$

or dividing through by $V$:

$$y_n = \frac{R}{V}x_{n+1} + \frac{P}{V}y_p.$$

Now $R/V$ and $P/V$ are assumed in any one case to be constants (in the example taken 74/100 and 26/100 respectively), and as $y_p$ is also a constant (in the example 90/100) consequently we have in this equation a straight line relation for the locus of a series of points whose coordinates are $y_n$ and $x_{n+1}$ respectively, and on the same diagram as was used (see Fig. 43) for the equilibrium relations of vapor and liquor, this same line may also be easily plotted as in Fig. 46.  Thus point $P$ is marked on the diagonal of the diagram where the perpendicular through 90 mol per cent cuts it, because at this point the vapor, reflux, and product all have this same concentration.  From this point we draw a line ($PC$) whose slope represents $R/V$, in our example having the value 74/100.  This is called the reflux line.  If we now draw a horizontal line representing vapor concentration 50 per cent to cut the equilibrium line $ABG$ in $B$ and the reflux line in $C$ and from these points drop perpendiculars to the base line at $S$ and $D$, we can read off that the liquor in equilibrium with the entering vapor would be about 30 per cent and the reflux that meets it is 34 per cent.  As $CD$ produced meets curve $ABG$ in point $I$ we can read at the left that the vapors leaving section $I$ have 55 mol per cent benzene and where a horizontal through $I$ cuts $CP$ in $I^1$ we read below that the reflex concentration is 40 mol per cent, which, in turn leads us on the ordinate to point 2 indicating vapors of 62 mol per cent, and so on stepwise we pass to point $2^1$ to 3 to $3^1$ and so forth.  Carrying on this process to the vicinity of point $P$ we find it would take 6½ such steps, each representing an ideal column section, to attain our goal of 90 mol per cent benzol with the assumed reflux.  If, in place of

drawing the line $PC$ on the equilibrium diagram, we draw it on a piece of transparent celluloid, we can readily (laying it over the diagram) shift its position to investigate the effect of varying the
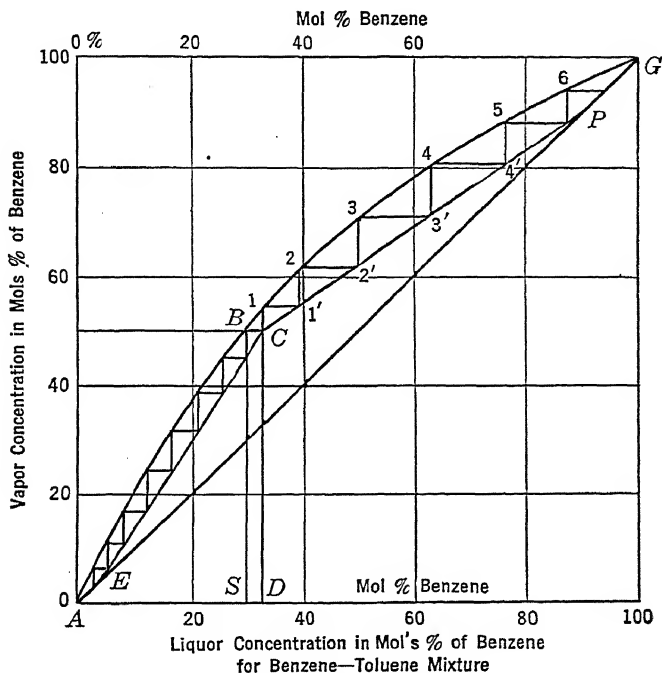


Fig. 46.   Equilibrium Relations of Vapor and Liquid.

concentration of the product (depending on the position of $P$) or the reflux ratio (on which depends the slope of the line $PC$). It must be noted that point $C$ must always be slightly to the right of point $B$.   If they coincided it would lead to the absurdity of an infinite number of steps, mostly of zero height, which is the condition at minimum reflux.   By shifting the reflux line as above described, it may be readily shown that to obtain higher concentration of product the most important point is to increase the number of column sections, while a diminution in the concentration of the feed must necessarily be met by increasing the slope of the reflux line.   If no product is taken off and everything is refluxed down the column, the reflux line coincides with the diagonal $AG$.   This condition is represented in Fig. 47.   In this

case $P = 0$ and $R/V = 1$ so $y_n = x_{n+1}$, that is, the composition of the vapor rising from a section is the same as that of the liquor returning in the reflux to it. If a column is so constructed
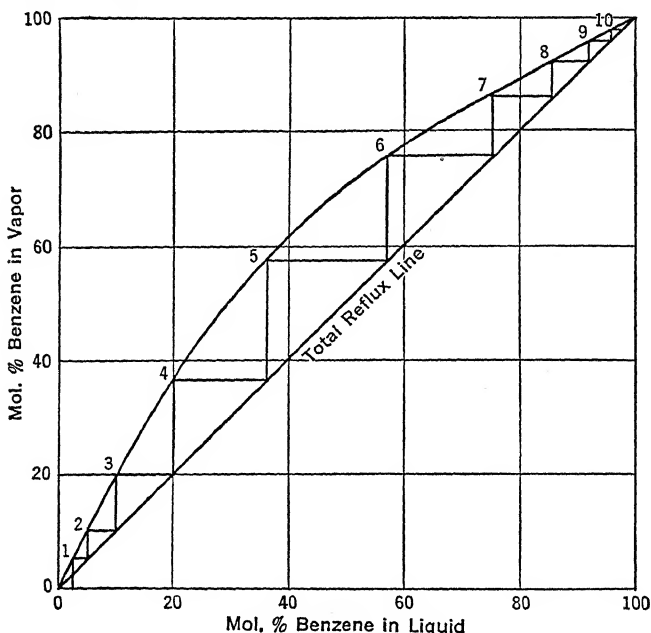


FIG. 47.   Effect of Total Reflux.

that samples can be taken and analyzed, either of the vapors or liquor at actual stages, by comparing the results with this diagram we can readily find out what number of actual plates or what height of packing is equivalent to an ideal column section. This will be discussed later.

**Exhausting Columns.** — In the above cases it is assumed that the flow down the column is either less than or equal to the vapors rising in amount. But another condition is possible in which a continuous stream of feed liquor enters a distilling column from some outside source exceeding in amount, either alone or with the addition of an internal reflux, the amount of vapors ascending in the same time. For the sake of simplicity we will assume that the feed has been preheated to the temperature of the column

where it enters and that the further internal heating in the column is negligible in amount. We also assume that the feed enters the column at a point where the reflux has the same concentration as it has. Using a similar notation to the preceding case and calling the amount of feed $F$ mols, we have a total reflux liquor below the feed of $F + R$ and if $F$ is large enough $(F + R)/V$ will be greater than 1. On the diagram (Fig. 46) from $C$ which point represents the feed and reflux composition at the entrance of the feed, a line $CE$ can be drawn whose slope is $(F + R)/V$. Suppose this line cuts the diagonal in a point $E$, this point would represent in our example a position in the column where the combined reflux only carries 4 mol per cent of benzene, and by drawing and counting the steps between the curve $AB$ and the line $EC$ starting at $C$ and $B$, we can find how many ideal sections it would take to reach the concentration of 4 per cent benzene, viz. $7\frac{1}{2}$ in this example. This will naturally vary as the concentration at $E$ is desired to be greater or less, and also as to the slope $(F + R)/V$ which can be modified by varying either $F$, $R$ or $V$. The effect of such changes on the number of ideal sections needed can be investigated by using a celluloid strip as in the case of the upper part of the diagram, to which this is analogous.

The above graphic method of computation regarding the internal behavior of distilling columns is due to McCabe and Thiele.[4] While some other methods may be more accurate and complete, the simplicity and directness of this one gives the clearest picture of the effects of the prime factors in fractionating.[5]

**Actual Distilling Columns.** — In the year 1801, a Frenchman named Adam started the line of improvements that resulted in the evolution of modern column stills. He conducted the vapors boiled off from a wine still beneath the surface of some cold wine in a second vessel and when this one also boiled, its vapors were conducted into more wine in a third vessel and so forth to a condenser. By these means he not only saved fuel by preheating the wine at no extra cost, but also obtained a stronger brandy than his competitors. This crude device led the way to more scientific attempts with the result that by the year 1818 there were in use improved stills with reflux condensers, and col-

[4] "Industrial and Engineering Chemistry," **17**, 605 (1925).
[5] B. V. Murphree, Industrial and Engineering Chemistry, **17**, 747 (1925).
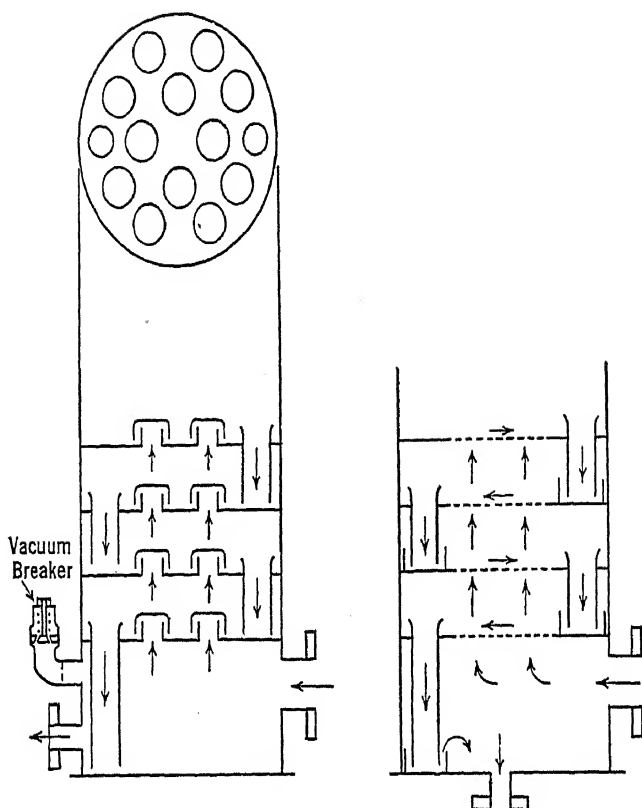
FIG. 48. Multiple Bubble Cap Columns.

or more inches apart, through which pass a number of short chimneys. Somewhat above each chimney is a cap of larger diameter which dips down into a pool of liquor retained on the plate. There are one or more overflow pipes to conduct any excess liquor from one plate to the next below. These project upward a sufficient distance to give the pool of liquor the desired depth, while the lower end is trapped in the pool below to prevent up-rush of vapors through it. The overflows of consecutive plates are generally on opposite sides of the column to give the

down flowing liquor the maximum length of travel and prolonged contact with the vapors escaping under the edges of the caps. The caps are commonly notched or serrated round their edges to subdivide the vapors better. A common cap diameter is 4″ to 6″. Often they are shaped like inverted troughs extending across the column. A vapor velocity of 20 feet per second is safe to allow in the chimneys, and 18″ per second velocity for the average vapor flow over the whole column section, when under atmospheric pressure.

*Sieve plate columns* have level flat plates somewhat like the above but the traps under their down pipes must be cup shaped to insure their holding liquor constantly. In place of caps and chimneys most of the plate area is pierced with holes a convenient mean size for which is about 3/16″ diameter spaced 1/2″ apart. The depth of liquor on the plate may be about 1″. Another type of sieve plate has fewer holes but each hole is D shaped with a tongue projecting from the straight side, leaving a C shaped slot. Both these types of plates are highly efficient and allow vapor velocities to be used of about 3 feet per second averaged over the column sectional area. They have not, however, as wide a range of allowable velocity as have capped columns and if the vapor velocity falls more than 50 per cent below the maximum the liquor drains through the perforations, and the efficiency is almost entirely lost.

**Testing the Efficiency of Plate Columns.** — This may be done by comparing the actual number of plates required to effect a certain separation, with the number of ideal sections required as indicated by the theory. Any plate column may be easily put to a test in this way if supplied with side drain cocks so that samples of liquor from a convenient number of plates may be drawn off, cooled, and analyzed. The simplest plan is to use total reflux under stable conditions and to sample every plate. This will enable us to count the actual stages needed to attain the same result as indicated by the diagram constructed from laboratory data. The results of such comparisons have shown efficiencies ranging from 40 to 70 or 80 per cent, the former for difficult separations, such as water from acetic acid, and the latter for easy ones, such as alcohol or acetone retification, and depending generally more on the material distilled than on column design.

**Packed Columns.** — These (see figure 49) are the modern version of the old trickle column with its conical baffles that alternately directed the flow of both vapor and liquor in and out from center to circumference and back in counter current. There is, in these columns, no definite pool or reflux liquor at any point but only thin streams, droplets, and films of liquor. The vapor travels in an upward direction counter current to the liquor, but both are continually forced to zigzag their direction of flow by meeting the filling bodies which are piled in at random. Hempel introduced the use of glass embroidery beads in laboratory columns of around 1″ in diameter and depended entirely on wall cooling to produce reflux. Ilges later used procelain balls around 1″ to 2″ diameter in regular plant columns, generally with internal reflux condensers. This type never had much vogue outside of Germany. Later Raschig introduced his rings, generally 1″ in diameter by 1″ long and made either of porcelain or metal, with such success that their use has been extensive. Various sizes are now used ranging from ½″ to 2″ or even 3″ diameter and length. Peters introduced rings cut from glass tubing ranging from 4 mm. to 12 mm. diameter that enable one to bridge the gap effectively between laboratory and plant sizes of columns, as it is necessary to have some reasonable ratio between the diameter of the column and that of the packing. It has, furthermore, been shown both practically and theoretically that as the ring diameter is increased the column height must increase in like proportion for a given fractionating effect.

Other varieties of filling bodies of the same general type are those of Prym and Lessing of whose behavior we have no data. Bregeat has recently brought out coiled wire spirals which allow higher vapor velocities to be used than the rings and also seem to give more efficiency for a given depth, but we have no exact data on these either.

As to the loss of pressure with various sizes of Raschig rings, Molinari has published the results given in Fig. 50.[6] The allowable velocities for a given column section are about the same for rings as for sieve plate columns, but are greater with larger than with smaller rings, as Molinari's data would indicate.

**Condensers and Dephlegmators.** — We have alluded to the necessity of reflux, and, of course, both this and the product must

[6] "Giorn de Chim. Ind. Applicata," 9, 276–281 (1927).

be condensed by cooling the vapor to below its boiling point. This is generally done either by passing the vapor through a tube immersed in water or by leading the vapor around a tube or tubes through which water flows. The choice between these plans depends mainly on convenience and cheapness, ease of cleaning, and practicable velocity of flow. The old style was an upright worm coil in a water tub. This is bulky and heavy and troublesome to clean, as the sluggish water flow generally involves deposits of slime that interfere with heat transfer. Upright multitubular condensers with water passing upwards through the tubes have become so common as to be almost standard. Even in these the water velocity is too slow to prevent slime gathering, but they are compact and easily cleaned. Multiple pass water tube horizontal condensers though much used in other fields have not been much used on stills, although the high water velocity obtainable with them reduces the necessary surface and prevents lodgment of slime.



Fig. 49. Packed Columns.

At times it is good to use an internal reflux either of coil or straight tube in the upper part of the column. These also can use high velocity of water flow and therefore small area of piping.

In many of the early types of stills, before the theory of the subject had been properly developed it was attempted to obtain a large part of the enrichment of the vapor by partial condensation, and sometimes to distribute partial condensers through the height and of the column between the plates. Both these ideas are now abandoned, the first largely as a result of the use of such efficient columns that practically nothing remains to be gained by fractional condensation, and the second because it is recognized that the more plates through which the vapor and reflux can interact the better, and condensing low down in the column merely wastes heat. In many cases it is now preferred
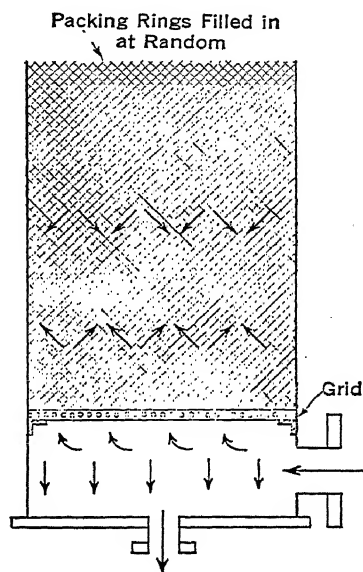
to use a single condenser both for reflux and product, and to control the amount going to product by a valve.    The water control is easier in this case as a slight excess does not upset a
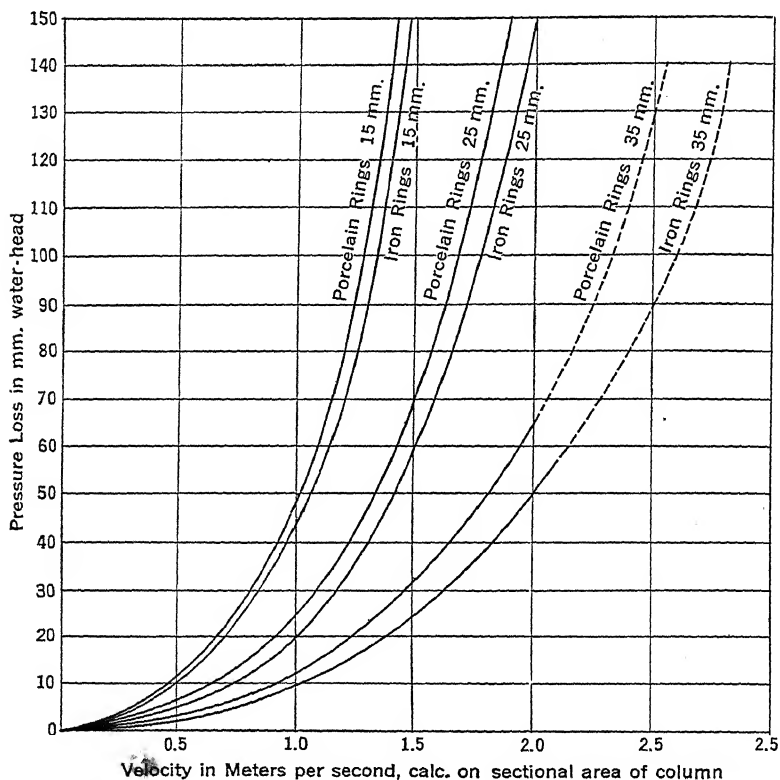


Fig. 50.    Pressure Loss in Columns Packed with Raschig Rings for Reflux of 6 Cubic Meters per Hour per Square Meter Section for Vapor Density of 1.2 Kg. per Cubic Meter.

nicely balanced proportion, as is generally the case with tandem condensers, in which the first condenses the reflux and the second the product.

Batch Stills. — A batch still is illustrated in Fig. 51.   It consists of these parts: the boiling vessel or still $A$, the fractionating column $B$ and the condenser $C$, besides minor accessories and

controls.   The boiler is generally heated by means of a coil supplied with pressure steam, regulated so as to be very steady and under exact control.   The boiler may be either horizontal or vertical.   The column is sometimes placed directly on the boiler, but it is somewhat more preferable to support it independently and to connect it with a suitable vapor line $D$ and a return pipe $E$ for the reflux. The proportion between hourly output and still capacity is a matter of convenience.   One seldom wishes to recharge a still more than once a day, while, with difficult separations, it is often desirable to run for several days without recharging.   The number of plates in the column may run from 10 to 50, according to the nature of the separation to be made, but a good average is 30 plates.   There is no great objection to sieve plates or packed columns with batch stills, as the column drainings find their way back to the boiler when operations are suspended, but in this case on starting up again, 30 minutes or more are needed after boiling starts to reprime the column effectively even when all the condensate is refluxed.

Batch stills are specially suitable for miscellaneous complex



Fig. 51.   Batch Still.

mixtures where there are three or more constituents and varying mixtures are handled from day to day.   Packed columns on batch stills have the special advantage that their hold-up of liquor while operating is so small that even when an ingredient may be present in small amount, it may be enough to give the conditions for good fractionation, while a plate column requiring
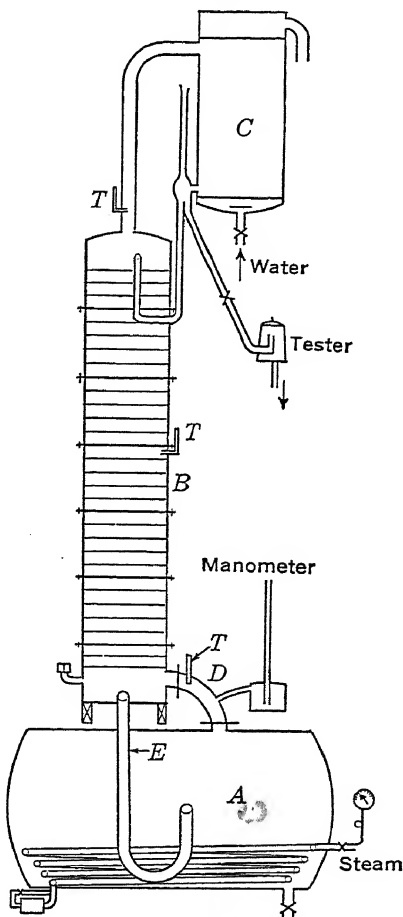
some 5 or 10 times as much liquid to load the plates can only function normally to give good fractionation when relatively large amounts of the ingredient are present. This results in closer " cuts " and less intermediates with packed columns of otherwise equal efficiency. The packed column is also advantageous as being self draining and easily washed or streamed out while the bubbler column is troublesome when changing from one material to another.

**Continuous Stills.** — A representative type of continuous still suitable for benzene is illustrated in Fig. 52. There is a feed tank $A$ to give a constant head and flow of feed liquor. This passes through a preheater $B$ shown as heated by the vapors and another $B'$ by the spent liquor from the base of the column. At $C$ is represented a preliminary or purifying column in which a first fraction of low boiling point (as hexane from benzene) may be distilled off, condensed in $H$ and the amount necessary to be removed taken off, at the heads tester. The heat is shown as supplied indirectly by steam in a calandria $F$, although in many other cases open steam is allowable if water is already present. The purified liquor flows down through the syphon trap $D$ into the main column $E$ which it enters somewhere near the center. In the lower part of the column $E$, the feed, mixed with the reflux, meets the vapors rising from the boiler $G$, also shown as indirectly heated. The boiling at this point has to be sufficient to expel the second ingredient (supposed in the example to be benzene) to the extent desired. At the top of the column vapors are taken off, of the concentrated product (benzene) often well over 99 per cent purity, through preheater $B$ and condenser $J$ to tester $N$. A reflux bottle $M$ insures that any condensate not allowed to flow to the tester must reflux down the column. Cooling water is supplied through valves at $K$ and $L$. The tails are shown as leaving the apparatus after partial cooling in the preheater. They would consist of impure toluene in the example. If pure toluene were required, another column would be required, or the impure product would be rectified in a batch still. Suitable thermometer locations are indicated by the letter $T$, and manometers with glass rising pipes are shown attached to the base of each column. These are to indicate any tendency of the columns to overload, thus raising the back pressure, a condition that must be met by diminishing the rate of feed or of
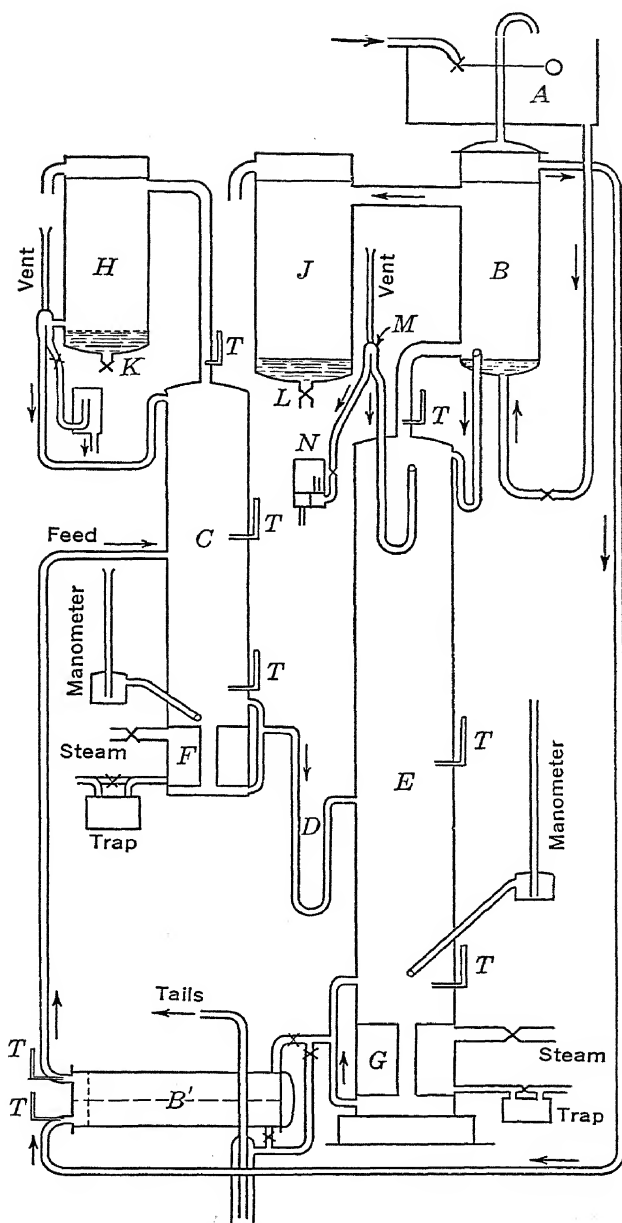
FIG. 52.  Continuous Still.

boiling, or of both. These manometers are charged with the same material as is present in the column. If large enough, they also serve as vacuum-breakers when closing down.

Continuous stills can be quite complex where there are several products involved, and require exact regulation of the various valves to maintain the temperatures at the correct points at which satisfactorily pure products result. However, when once started up they are not generally difficult to operate. Their great advantage over batch stills is in giving larger yields of pure products and cutting out intermediate fractions. They also use less steam for a given output.

### PROBLEMS

15. Plot the vapor pressure curves of methyl and ethyl chlorides as given on page 231, Vol. III, Int. Crit. Tables, using log $T$ versus $1/T$ paper and from these graphs determine the boiling points of each under 2 atm. pressure and 20 atm. pressure.

16. Calculate graphically the number of theoretical plates necessary in the problem illustrated by Fig. 46 if the product is to be 99 wt. per cent benzene and the waste 1 ml. per cent toluene if the reflux ratio were 3.1? What result if the reflux ratio were 10.1? How many actual plates will be required in each of the above examples if the plate efficiency were 62 per cent?

17. What type still would you prefer for the following distillations: A two component system of uniform composition? A multicomponent system of varying analysis? Various unknown compositions?

18. What diameter should the columns in Problem 16 have, if the feed rate is 1000 lbs. per hour, and the mean vapor velocity employed were 1.4 feet per second at atmospheric pressure?

# CHAPTER V

## STEAM DISTILLATION

### THEORY AND PRACTICE

JAMES W. LAWRIE, Ph.D.

By the term " Steam distillation " is meant the production of a mixed vapor consisting of steam and the vapor of the substance being distilled. The steam may be generated from water present in the system or introduced as such. Heat other than that furnished by the steam must generally be supplied in order to volatilize the substance being distilled.

Steam distillation is advantageous when high boiling substances must be distilled, as the injection of steam into the still reduces the temperature of distillation greatly and carries over the vapors of the substances being distilled. The distillation temperature may be reduced further by carrying out the operation in a vacuum. Substances which are subject to decomposition when distilled alone may often be distilled without decomposition with steam at atmospheric pressure or in a vacuum. In order more fully to understand the value and application of steam distillation it is necessary to discuss its theory.

**Immiscible Substances.** — Steam distillation is most readily applied to immiscible substances whether liquid or solid. When two immiscible substances are brought together and heated to a given temperature, each substance produces the same vapor pressure which it would produce at that temperature if alone. The total vapor pressure produced will be the sum of the vapor pressures of the two substances. If one of these substances is water and the operation is carried out at atmospheric pressure, distillation will occur at a temperature below the boiling point of water (100° C.) because the total vapor pressure cannot exceed 760 mm. If the second substance boils below 100° C. steam distillation will take place below its boiling point, that is, the boiling point of a mixture of two non-miscible liquids must be lower than the boiling point of either substance. For instance,

135

benzene has a boiling point at 760 mm. pressure of 80.2° C., water at the same temperature boils at 100° C., while the mixture boils at 69.2° C. at 760 mm. pressure. At 69.2° benzene has a vapor presure of 535 mm. and water 225 mm.

The amount of each substance carried over will be a function of the vapor pressure and the molecular weight of the substances. In the illustration given above, as the molecular weight of benzene is 78 and that of water 18, the relative amounts by weight of benzene and steam in the mixed vapor will be $535 \times 78$ to $225 \times 18$, or 41,730 parts of benzene to 4050 parts of water. As most substances which are steam distilled have high molecular weights, while water has a low molecular weight, the amount of steam required per pound of substance distilled is generally not high even though the vapor pressure of the substance distilled at the temperature of distillation is comparatively low.

**Miscible Substances.** — When two liquids are completely miscible in each other, such as glycerol [1] and water, the partial vapor pressure of each in the mixed liquid is lower than the vapor pressure of each separately at the same temperature and, therefore, the boiling point is higher than that of the lower boiling component.

When a solution of glycerol in water is heated, the vapor consists of steam and glycerol vapor. As the water is the more volatile substance, it passes off in the greater proportion, the percentage of glycerol in the liquid, as well as the boiling temperature, rising rapidly until the boiling point of pure glycerol (290° C.) is reached, when pure glycerol vapor is produced. Considerable decomposition of glycerol takes place at this temperature. The distilling temperature may be reduced by reducing the pressure and distilling in a partial vacuum. The boiling point of glycerol is 210° C. (410° F.) at 50 mm. pressure and 179.5° C. (355° F.) at 12.5 mm. It would be very difficult to maintain a vacuum at 12.5 mm. in commercial apparatus, but by introducing steam superheated to 180° C. it is possible to distill glycerol at 180° C. at 50 mm. (2 in. mercury) pressure, which is entirely feasible commercially. Under these conditions the vapor tension of water vapor would be 37.5 mm. and of

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[1] The term "glycerol" is used in preference to "glycerin" as glycerol is an alcohol and the ending "ol" has been adopted as the scientific terminology for alcohols. The term "glycerin" is used commercially for dynamite grade glycerol.

glycerol 12.5 mm.   The relative weights of glycerol and water vapor under these conditions would be 1150 and 675.

**Distilling Pressure.** — The choice of distilling under reduced pressure, atmospheric or increased pressure, is dependent on the nature of the materials being distilled, the cost of distillation, and the yields required.   It is almost essential that some materials be distilled under reduced pressure because at normal or increased pressures many materials undergo serious decomposition. On the other hand, there are many low boiling substances whose recovery by condensation would be most difficult if distilled under reduced pressures.   Thus ether, acetone, ethyl alcohol, and other low boiling substances are practically never distilled under vacuum because of the difficulty of condensing the vapors, the average temperature of the water used in the condensers being above the boiling points of these substances at low pressures.   If, however, the effect of higher boiling temperature is not harmful, an increase in pressure may sometimes be advantageous. Steam distillation is somewhat similar to distillation under reduced pressure, for the law of partial pressures is applicable and the substances distilled with steam only attain the temperature corresponding to their partial pressures.   Thus, benzaldehyde boils at 178.07° C. (Table I) under 760 mm. presure, but when

TABLE I.—VAPOR PRESSURES OF STEAM AND BENZALDEHYDE AND BENZENE AT VARYING PRESSURES

|  | Total Pressure mm. | Partial Pressure in mm. | | Temp. °C. | Per Cent by Weight |
|---|---|---|---|---|---|
|  |  | Water | Substance |  |  |
| Benzaldehyde boiling point 178.07° C. at 760 mm. | 76.1 | 72.5 | 3.6 | 45.3 | 22.5 |
|  | 762.5 | 706.0 | 56.5 | 97.9 | 31.4 |
|  | 3040.0 | 2772.0 | 268.0 | 140.7 | 38.2 |
| Benzene boiling point 80.2° C. at 760 mm. | 76.0 | 13.5 | 62.5 | 16.0 | 95.3 |
|  | 760.0 | 225.0 | 535.0 | 69.2 | 91.0 |
|  | 3040.0 | 1173.0 | 1867.0 | 112.6 | 86.9 |

steam distilled, it boils at 97.9° C., the corresponding partial pressure being 56.5 mm., or a reduction of 760 − 56.5 = 703.5

mm. The per cent by weight of benzaldehyde in the vapors is 31.4. If the distillation is carried out with steam under reduced pressure of 76.1 mm. Hg, then the partial pressure of benzaldehyde is only 3.6 mm. and the per cent by weight in the vapors is only 22.5, but under a pressure of 3040.0 mm., the per cent in the vapors increases to 38.2. If the boiling point of the liquid under normal pressure is only a little lower than that of water, at the same pressure, the vapor becomes poorer in the liquid being steam distilled, as the pressure is increased. This is shown in the case of benzene.

In the case of benzaldehyde, the steam consumption per kg. under 762.5 mm. is

$$\frac{100 - 31.4}{31.4} = 2.18 \text{ kg.}$$

If the pressure is 76.1 mm., the steam used is

$$\frac{100 - 22.5}{22.5} = 3.44 \text{ kg.}$$

and at 3040 mm., the steam used is

$$\frac{100 - 38.2}{38.2} = 1.61 \text{ kg.}$$

or less than half that required at 76.1 mm. For benzene, we have the steam consumptions per kilo as follows:

| | |
|---|---|
| 76 mm. | 0.049 kilos |
| 760 mm. | 0.099 kilos |
| 3040 mm. | 0.15 kilos |

or a large increase proportionately with increase in pressure.

**Temperature Drop in Steam.** — In steam distillations made under reduced pressures, if the steam is fed to the still under pressure, and it immediately expands under the reduced pressure in the still, there is always a drop in temperature of the steam under the reduced pressure. This loss in temperature is often quite large, as may be seen from the following table (II).

TABLE II.—DROP IN TEMPERATURE DUE TO EXPANSION OF STEAM

| Initial Pressure Lb. sq. inch | Initial Temperature °C. | Temperature after Expansion | |
|---|---|---|---|
| | | to 760 mm. °C. | to 76 mm. °C. |
| 14 | 100.00 | 100.0 | 83.3 |
| 21 | 111.74 | 108.1 | 91.4 |
| 28 | 120.60 | 113.4 | 96.7 |
| 42 | 133.91 | 121.9 | 105.2 |
| 56 | 144.00 | 128.2 | 111.5 |
| 70 | 152.22 | 133.3 | 116.6 |
| 84 | 159.22 | 137.7 | 121.0 |
| 98 | 165.34 | 141.4 | 124.7 |
| 112 | 170.81 | 144.8 | 128.1 |
| 126 | 175.77 | 147.9 | 131.2 |
| 140 | 180.31 | 150.7 | 133.9 |

This drop in temperature may be calculated by use of Zeuner's equation [2] which is

$$pV = \text{B.T.} - Cp^n,$$

where $B$, $C$ and $n$ are constants, and

$$\frac{C}{B} = 38.11, \qquad n = 0.25,$$

$p$ being the pressure in atmospheres, $V$ the volume in cubic meters per kilogram, and $T$ temperature in °C.

If the steam has the initial temperature of $T_1$ at a pressure of $p_1$, and a volume $v_1$, and it be released to a still at $T_2 . p_2$ and $V_2$ respectively, then

$$p_1 v_1 = p_2 v_2 = BT_1 - Cp_1^n = BT_2 - Cp_2^n,$$

whence

$$T_1 - T_2 = \frac{C}{B}(p_1^n - p_2^n).$$

For example, if we consider steam at 70 lbs. per square inch pressure (5 atmospheres) introduced into a still at one atmos-

[2] Technische Thermodynamick, 2, 221, 1900.

phere pressure, we have

$$152.22° \text{ C.} - T_2 = 38.11 \, (5.25° - 1.25°),$$
$$T_2 = 133.3° \text{ C.}$$

The loss in temperature is, therefore, 18.92° C.

If superheated steam is used in place of saturated steam in a still at ordinary pressure (760 mm.) there is less condensation due to heat radiation losses, the superheat causing some of the water to evaporate, but no gain beyond this over regular steam will result as long as condensed water is present in the still. If all condensation of steam is prevented, the higher temperature of superheated steam will cause an increase of the proportion of the distilled substance in the distillate. Thus, if we use super-heated steam, equivalent in temperature to steam at a pressure of five atmospheres, to distill benzaldehyde at atmospheric pressure, and allow no condensation to take place in the still, the vapor pressure of benzaldehyde is 220 mm., the total pressure is 760 mm., and the steam vapor pressure is 540 mm. The proportion of benzaldehyde in the vapors will be 70.6 per cent whereas with steam at 100° and 760 mm., the distillate will contain only 31.4 per cent benzaldehyde.

**Distillation of Immiscible Liquids.** — Dalton's law states that when two or more gases, or vapors, which do not react chemically with one another are mixed, each gas exerts the same pressure as if it alone were present and that the sum of these pressures is equal to the total pressure of the system, thus

$$P = p_1 + p_2 + p_3 + \text{etc.,}$$

in which $P$ = total pressure, and $p_1$, $p_2$, etc., are the pressures of the components.

**Boiling Point.** — If a mixture of immiscible liquids, such as water and a volatile oil, is distilled, the boiling point of the mixture is that temperature at which the sum of the vapor pressures of the components is equal to the total pressure in the system. This temperature is necessarily lower than the boiling point of the most volatile constituent. The boiling point of the mixture remains constant until one of the constituents has been almost completely removed, when the boiling point rises rather suddenly to that of the liquid remaining in the still. The vapor

coming from such a mixture contains all the components in proportion by volume to the relative vapor pressure of each component, and the distillate contains all the components of the original mixture. As the liquids are immiscible, separation is generally easily effected. A steam distillation of this kind is carried out for the purpose of separating a given substance from non-volatile impurities or reagents used in its preparation.

**Relative Quantities Distilled.** — If $P_A$ and $P_B$ are the vapor pressures of two completely immiscible liquids, $A$ and $B$, at $t°$, the two substances will distill over proportionately to their vapor pressures, $P_A : P_B$, by volume of vapor. If $D_A$ and $D_B$ are the respective densities of the two vapors at the boiling point of the mixture, the relative quantities by weight $M_A^1$ and $M_B^1$ will be

$$\frac{M_A^1}{M_B^1} \quad \frac{P_A D_A}{P_B D_B},$$

and, inasmuch as the vapor density of a substance is a function of its molecular weight, it is possible to calculate the weights of the two components that distill over from a knowledge of their molecular weights and their vapor pressures at the boiling point of the mixture. Thus

$$\frac{M_A^1}{M_B^1} = \frac{P_A M_A}{P_B M_B},$$

and the mixed vapor will consist of

$$\frac{P_A M_A}{P_A + P_\jmath} \text{ of } A, \quad \text{and} \quad \frac{P_B M_B}{P_A + P_B} \text{ of } B.$$

According to Dalton's law, one liter of the mixed vapors will contain one liter of each component at its partial pressure and the weights of these components will be

$$\frac{M \times 273 \times P}{22.4 \times (273 + t) \times 760}$$

in which $M$ is the molecular weight of the particular component, and $P$ is its vapor pressure at the temperature $t$.

If we have the molecular weight of a substance, and its vapor pressure at a known temperature, it is possible to calculate

approximately the weight of the substance which will distill over with steam.

If we take as an example the distillation of benzaldehyde with steam, assuming the temperature to be 100° C., and the pressure as 760 mm., the molecular weight of benzaldehyde is 106, and its vapor pressure $P_B$ at 100° C. is 61 mm.   The partial pressures of water $P_A$, and benzaldehyde $P_B$ are given by the equations:

$$P_A = \frac{P_A{}^1 \times 760}{P_A{}^1 + P_B{}^1} \quad \frac{760 \times 760}{760 + 61} = 703.5$$

for water and

$$P_B = \frac{P_B{}^1 \times 760}{\cdot + P_B{}^1} \quad \frac{61 \times 760}{760 + 61} = 56.5$$

for benzaldehyde.

$$P_A + P_B = 703.5 + 56.5 = 760.$$

If we substitute the above values in the equation:

$$\frac{M_A{}^1}{M_B{}^1} = \frac{M_A P_A}{M_B P_B},$$

we have 12,670/5988 and bringing to per cent, this gives 68/32, so the distillate contains 68 per cent water, and 32 per cent benzaldehyde.

The relation $M_A{}^1 : M_B{}^1 :: M_A P_A : M_B P_B$ indicates the great value of steam distillation, since the smaller the product $M_A P_A$, the larger is the value of $M_B{}^1$.   Water with its low molecular weight and relatively moderate vapor pressure has a low value for $MP$, mass times vapor pressure.

The specific heat of water at 0° is 1.0093; at 80° C. it is 1.0017; at 15°, 1.000.   In general, the specific heat of any substance is different at different temperatures.

The specific heat of mixtures can be approximately calculated from the specific heats of the components.   Thus, if $C$ is the specific heat of the mixture, $C_A$ and $C_B$ the specific heats of the components, and $W_A$ and $W_B$ the weights of the components, then

$$C = \frac{C_A W_A + C_B W_B}{W_A + W_B}$$

The differences between the calculated and observed is usually very small, but in some instances is considerable.

**Latent Heat of Vaporization.** — The change of liquid to vapor is accompanied by a considerable amount of heat absorption. If the vaporization is conducted under constant pressure, and if the vapor is of uniform composition, the temperatures of the liquid and vapor are the same. The latent heat can be calculated approximately by the use of the law $ML/T = $ constant (20.5) where $M = $ molecular boiling point, $T$ is absolute temperature, and $L$ is latent heat of vaporization expressed in calories per gram. This is known as Trouton's law [3] and points out that the value of $ML/T$ is nearly identical for many liquids when compared at atmospheric pressure.

The latent heat of vaporization of many substances have been determined experimentally and may be found in suitable reference books.[4]

The vapor tensions of many substances have been determined at various temperatures so that the partial pressures of these substances when distilled with steam at varying pressures and their temperatures is known.[5]

While the behavior of many single or mixed substances on distillation may be ascertained by a study of their physical properties, it is often desirable to carry out laboratory tests in order to verify the conclusion reached and also to learn the effect of impurities which may be present in greater or smaller amounts. For this purpose a description of laboratory distillation and fractionation equipment is given at the close of this chapter.

## DISTILLATION OF GLYCEROL

In the latter part of the last century, glycerol was recovered largely by evaporation of sweet waters from the production of stearin for tallow candle manufacture and from soap lyes. This glycerol was very impure. In 1854 C. F. Wilson [6] made the first distillation of glycerol from candle and soap lye crudes. He did not use any steam or vacuum, but had water present in the crudes and so got a lowering of the vapor pressure. The yields were low. Wilson and Payne improved upon this method by

[3] Hildebrand, Phil. Mag., **18**, 54, 1884; Journal American Chemical Society, **37**, 970, 1915.

[4] Table 221, Van Nostrand's Chemical Annual, gives latent heat of vaporization of a number of substances at various temperatures.

[5] See tables 192 and 196, Van Nostrand's Chemical Annual.

[6] British Patent 1624, 1854.

passing a current of steam through the crude, which removed volatile acids. Then the steam was superheated and the temperature of the liquid in the still was raised until the glycerol distilled over. It was not until 1881 that O'Farrell patented the use of vacuum together with steam for the distillation of glycerol. His process was also the first continuous method for the recovery of glycerol, as he provided two sets of receivers for the distillate, so that when one receiver was filled it could be shut off from the system, emptied and the second receiver turned open to the system.

**Fractional Condensation.** — W. Clark [7] in 1881 introduced the idea of fractional condensation of glycerol from the vapors coming from the still and was able to obtain a fairly pure glycerol of almost 98 per cent strength by maintaining the condenser at a high temperature. In 1882 Payne [8] used a condenser maintained at a temperature of 150–200° C. which brought the glycerol, to practically 99–100 per cent strength. It is obvious that at these high temperatures very little water will condense while a large amount of the glycerol which has a boiling point of 290° C. at 760 mm. will become liquid. The fractional condensation of glycerol by means of high temperature condensers is now utilized in all glycerol distillation systems. The high temperature is maintained either by using air condensers or hot water condensers.

**Steam Heated Stills.** — The next big improvement in glycerol distillation was made by Van Ruymbeke [9] in 1894. Up to this time the stills used in glycerol distillations had been heated by a direct fire on the bottoms of the stills. This resulted in considerable decomposition of the glycerol, and gave rise to the production of acrolein, glycerol ethers, and gave a distillate of poor color, etc.

Van Ruymbeke introduced the use of steam as the sole source of heat for distillation. This improvement increased the yield of glycerol and also gave a purer product. It was rendered possible by the lowering of the distillation temperature due to the use of vacuum and steam for distillation. The fuel consumption was

[7] British Patent 5384, 1881.
[8] British Patent 203, 1882.
[9] U. S. Patent 522,132, 522,135, 1894.

also reduced because the steam boiler utilizes a much higher percentage of the heat value of coal than a glycerine still. The Van Ruymbeke process is still being used to a very large extent throughout the world, and is the first of the modern processes.

**Classification of Distillation Methods.** — The modern methods of glycerol distillation may be divided into three large classes, each with its subdivisions:

1. The open system.
2. The closed system.
3. The flash system.

Under the open system may be classed all of the processes in which the sweet water or liquor condensed after the bulk of the glycerol is removed from the distillation vapors, is recovered and does not again, as such, reenter the distilling system.

With the closed system the sweet-waters are run back into an evaporator and the vapors, driven off during the concentration of these sweet waters, pass from the evaporator into the glycerol still after passing through heat exchangers where they are superheated, while greatly expanded due to being under vacuum, by the glycerol steam vapors coming from the glycerol still. The Wurster-Sanger system is an example of the closed method. It will be described later.

The best example of the flash system is the Wood method of distilling glycerol. In this equipment the glycerol is distilled in a series of stills, each at a slightly higher vacuum than the preceeding still. The glycerol undistilled from one still passes into a heat exchanger where it is reheated above the boiling point and is flashed into the next still. The Wood system uses from three to six stills in a series.

**The Open System of Glycerol Distillation.** — The Van Ruymbeke system is the outstanding example of the open class. The open system has the advantage of the complete removal from the distillation system of all of the low boiling impurities. Until a few years ago this was extremely important, because the purification of crude glycerols was not as far advanced as it is today, and until better methods of clarification were introduced the open system alone produced the highest quality of glycerol.

Van Ruymbeke avoided the local overheating of the direct

fire-heated still by using boiler steam at a pressure of 175 to 200 pounds. This steam was expanded from boiler pressure to the reduced pressure used in the still, but before entering the still was reheated to the same temperature as the boiler steam. In this way, the sensible heat lost in expanding was replaced and steam under high vacuum, but at the optimum temperature for distillation of glycerol under high vacuum, was obtained. The result of this procedure was a large increase in the distillation yields over the old methods and the production of glycerol of a much higher purity.

*Jobbins-Van Ruymbeke Still.* — Figure 53 gives a side elevation of a Jobbins-Van Ruymbeke still (so called as it was first used at
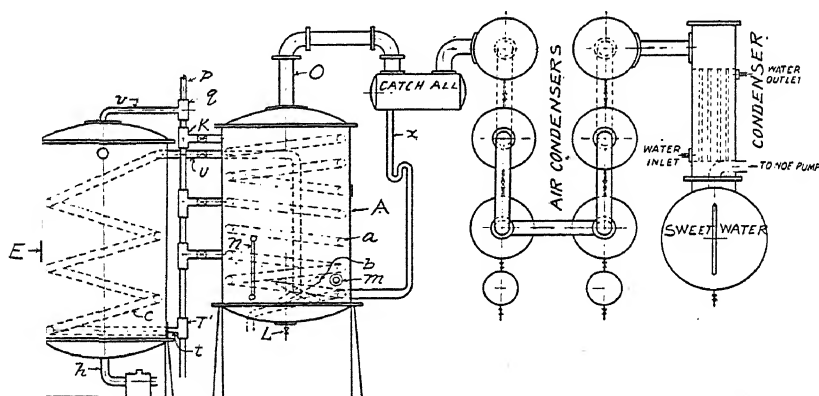


FIG. 53. Van Rymbeke Still.

the Glycerol Refinery of Wm. F. Jobbins, Inc., of Aurora, Ill.). In the figure, $A$ is the still, $E$ is the steam expander and reheater which produces superheated steam. The catchall is a baffle box to remove entrained material, the air condensers separate the glycerol from the steam vapors and the final cold water condenser produces the sweet waters. Steam enters $E$ at $t$ through a small pipe controlled by a valve. Pipe $t$ connects directly into pipe $C$ which is about $3''$ in diameter. Pipe $C$ is a series of coils of about the same diameter as the tank and the coils are set about one inch apart. In addition, a cone basket of coils at the top and bottom of the tank are often used. As the steam entering pipe $C$ passes through the coils at high velocity, it is necessary to have a very large surface in order to reheat it in the short time

available. Therefore, a large number of coils are used. At $V$ free steam from the boilers enters tank $E$ and is maintained at close to boiler pressure, and, therefore, also close to the temperature of steam at the boiler pressure. The condensate from this steam passes to a pressure trap through pipe $h$. The steam in coil $C$ is, therefore, expanded and reheated before it enters the still $A$ through the pipe $U$ and sparger $b$.[10]

The still $A$ consists of a steel tank usually 7 to 8 feet in diameter and 8 to 10 feet high on the straight edge. It is lined inside with a series of coils of 2 to $2\frac{1}{2}''$ pipe. The coils should be of such a length that the temperature available from the high pressure steam near the end of the coil is not less than the temperature of the vapors leaving the still. It is, therefore, essential to divide the total coils of the still into proper lengths. The steam can enter these coils through a header and leave the outlet ends either to separate traps or through a second header to a single pressure trap. The outlet end of the header can also be tapped so that there is a flow of steam to the evaporators where the sweet waters and low gravity glycerol are concentrated. The purpose of extending these coils above the surface of the charge of glycerol is only to keep the vapors of glycerol and steam at such a temperature that there will be no condensation of glycerol from the vapors inside of the still.

*Operation.* — In operating the still, crude glycerol of high concentrations (80 to 90 per cent), is drawn by vacuum from the feed tank in which the crude is kept at 100–110° C. The still is filled about one-third full, vacuum is brought as high as possible (28–29 inches), steam is turned into the preheater tank $E$ and the coils $A$ in the still. When the water in the crude is largely evaporated and glycerol is about to start to distill, steam is turned into the coils $C$ of the superheater and passes through the sparger $b$ into the charge of crude in the still. The hot vapors heat up the piping, catchall and air condensers. Until these parts of the equipment are at proper temperature, the glycerol separating in each will be dilute and is usually returned either to the still or sent to the concentrator. When the still is operating at the proper temperature, the glycerol from the first three air condensers usually averages 99 per cent in strength. That from

[10] The cross pipes where the superheated steam enters the still under the surface of the glycerol in the still are called the sparger or spider.

the last condensers is more dilute and must be concentrated to a strength of 99 per cent.

E. T. Webb [11] describes the performance of a Van Ruymbeke still used at the Gretna factory in England. With an eight-foot diameter cast-iron still, using a three-inch steam coil and steam at 240 pounds gauge pressure and connected to twelve air condensers, ten feet by three feet, arranged in three columns of four condensers each, ten (British) tons of crude glycerol are distilled in from twenty-two to twenty-four hours. When the still is started, there is a large condensation of weak distillate in the air condensers. It takes about two hours' time to get the system heated to proper temperature so that the condensate is of high gravity and the volatile impurities pass on with the hot steam vapors. The condensate for this preliminary period is returned to the still. The temperatures observed in the various air condensers during the distillation proper are given as follows:

| | |
|---|---|
| (1) 387° F. | (7) 320° F. |
| (2) 382° F. | (8) 300° F. |
| (3) 375° F. | (9) 252° F. |
| (4) 365° F. | (10) 223° F. |
| (5) 352° F. | (11) 193° F. |
| (6) 337° F. | (12) 161° F. |

The average temperatures of the 3 columns of condensers are:

(1) 356° F. (Condensers 1–2–3–4),
(2) 348° F. (Condensers 5–6–7–8),
(3) 207° F. (Condensers 9–10–11–12).

*Distillate.* — The rates at which the distillate collects in the receiving drums under each column of condensers is:

(1) 530 pounds per hour.
(2) 420 pounds per hour.
(3) 200 pounds per hour.

This would seem to indicate that Column 3 yields 17.4 per cent of the total glycerol recovered, whereas it actually yields only 10 to 12 per cent because of the longer period required to heat up the condensers in the third column. The glycerol receivers at the base of each column of air condensers are fitted with pressure steam coils to evaporate the condensate to a high gravity; that

[11] Perfumery and Essential Oil Record, **17**, 284, 1926.

in Column 1 having a specific gravity of approximately 1.263–1.2635 (99–99.3 per cent), in Column 2, 1.2625–1.2630 (99.1–98.9 per cent) and in Column 3, 1.2540–1.2560 (95.6–96.4 per cent). Any trimethylene glycol in the crude is recovered in Column 3 and its presence lowers the gravity of the condensate from this column.

*Sweet Water.* — The weight of sweet waters produced is approximately 1.2 pounds per pound of 80 per cent soap-lye crude, and 1.0 to 1.05 pounds per pound of saponification crude. The concentration of the sweet waters is usually 2 to 3 per cent glycerol. As the amount of foots accumulates in the still, the rate of distillation gradually falls off with a lowering in temperatures of the vapors, and it is, therefore, necessary to increase the amount of free steam entering the still.

With a soap-lye crude containing 7.6 per cent organic residue, 95 per cent of the total volatile impurities were condensed by the water-cooled tubular condensers along with the sweet waters. The sweet waters are, therefore, evaporated separately to about 40 to 50 per cent concentration when they are boiled with a slight excess of caustic soda and given a treatment of 5 pounds of char per ton of liquor. They are then filtered and the filtrate is concentrated to 80 to 90 per cent strength and distilled separately. The sweet waters from the distillation of the treated concentrated sweet waters is rich (up to 30 per cent) in trimethylene glycol, which may be recovered, after concentration, by fractional distillation.

*Foots.* — The foots are dissolved in water and treated with iron salts to precipitate fatty acids. They are then neutralized with caustic soda to precipitate excess iron salts, refiltered and evaporated in a salt-pan evaporator. The concentrate is then distilled and the distillate is added to the regular crudes being distilled.

*Yield.* — The approximate recoveries of the Van Ruymbeke stills at Gretna, England, are given:

|  | *Weight in Terms of 100 Per Cent Glycerol (Tons)* | *Yield* |
|---|---|---|
| Total quantity of 80 per cent curde charged... | 8.00 | 92.4% |
| Recovered as refined glycerol (99 per cent) .... | 7.393 | 5.7% |
| In sweet waters............................ | 0.456 | 1.9% |
| In foots................................... | 0.151 |  |

*The steam consumption* was 4.5 pounds per pound of crude

glycerol using single-effect evaporators for concentrating the sweet waters. (This steam consumption is rather high as many plants use as little as 3 pounds for all operations.) The heat balance for distilling 100 tons of soap-lye crude (80 per cent) is given in Table IV.

TABLE IV.—HEAT BALANCE IN THE VAN RUYMBEKE STILL

| Steam Input | Tons | Steam Consumed | Tons |
|---|---|---|---|
| Steam to closed coil............ | 75.90 | Latent heat to glycerol........ | 12.34 |
| Free steam through spider...... | 106.40 | Sensible heat to glycerol....... | 12.64 |
| | | Evaporated water........... | 7.21 |
| | | Injected steam............... | 112.03 |
| | | Radiation................... | 35.61 |
| | | Foots...................... | 2.47 |
| | 182.30 | | 182.30 |

Briggs [12] gives some additional figures for the operation of the Van Ruymbeke process in Great Britain. He states that the distilled glycerol collecting in the first air condenser receiver amounted to twice that which is collected in the second condenser. The condensate from the first receiver had a specific gravity of 1.26, that from the second 1.240. The average from the entire distillate was 1.253, having a strength of about 95 per cent. The sweet waters had a weight equal to the weight of the crude charged into the still and contained about 10 per cent glycerol. The recovery yields were:

Weight of glycerol charged to the still, 14,926 pounds of 82.8 per cent strength, equal to 12,350 pounds of 100 per cent glycerol.

| Recoveries | Pounds | Glycerol Content | Yield |
|---|---|---|---|
| Storage.................. | 10,850 | 97.5% | 85.7% |
| Weaks.................. | 13,800 | 9.2 | 10.3 |
| Foots.................. | 2,300 | 14.2 | 2.6 |
| | | | 98.6% |
| Loss............... | | | 1.4 |

[12] Distilling Principles and Processes, Sidney Young, MacMillan & Co., p. 425, 1922.

The duration of the test was 42 hours, steam pressure 180 pounds per square inch and vacuum 1.6 inches absolute pressure. The fuel consumption was about 0.55 pound of coal per pound of crude charged or about $0.55 \times 7 = 3.85$ pounds of steam which includes steam for vacuum pumps, still, concentrator, etc.

The quality of glycerol produced by the Van Ruymbeke process when properly carried out is of the highest grade. The solids entrained by the vapors from the still and materials of higher boiling point than glycerol which may be distilled are separated in the catchall from the glycerol steam vapors, and are returned to the still, or may be sent to a separate tank. Substances having a low boiling point are carried on through the system and are finally condensed with the sweet waters, which should be of such glycerol strength as to have no value. In this way, any obnoxious impurities distilling over with the glycerol are removed permanently from the system and do not accumulate either in the still or in the sweet waters.

**Closed System of Glycerol Distillation.** — As we have already mentioned, the soap maker has learned to improve the method of purifying his soap lyes so that today it is no longer essential to use the open system of distillation in order to get glycerol of sufficient purity to be used for making dynamite. In order to effect economies in the amount of steam required, the so-called closed system was developed by Garrique and also by Wurster and Sanger. These systems are almost identical in general principles and differ from each other only in some details.

The *Wurster-Sanger* equipment is now being used very largely in the newer plant installations. Their equipment and process will, therefore, be discussed. In general, however, the description will also fit the *Garrique* method and equipment. These two systems are the best examples of the closed method for distilling glycerol. In the closed method the sweet waters, until just recently, have been returned to the evaporation and distilling systems and, therefore, there was an accumulation of lower boiling impurities which were always present in the system, while distillation was carried on. Wurster and Sanger have overcome this objection in their newest equipment by the use of a second sweet-water evaporator. This is shown in Fig. 54 and its use and value are described below. Moreover, due to the very efficient modern methods of chemically treating weak soap lye crudes,
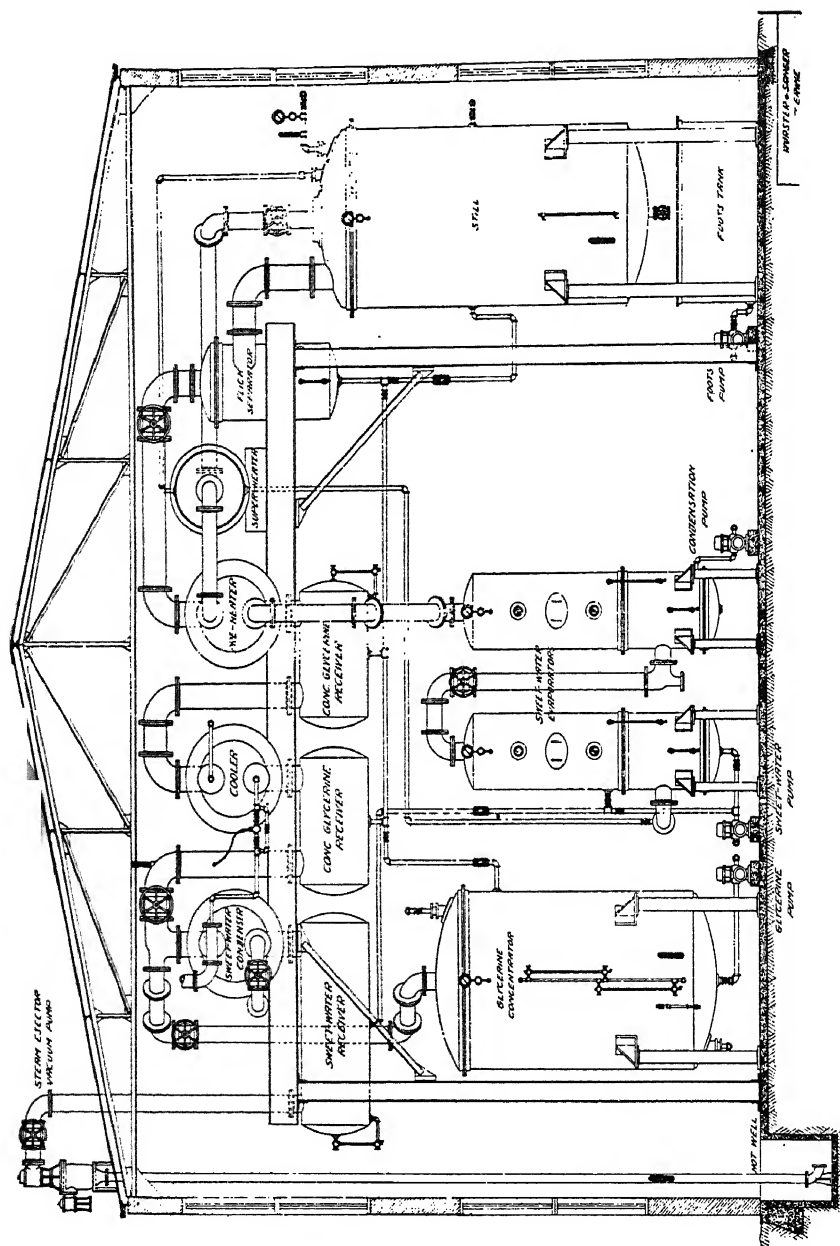
FIG. 54.   Wurster and Sanger Glycerine Distillation Plant.
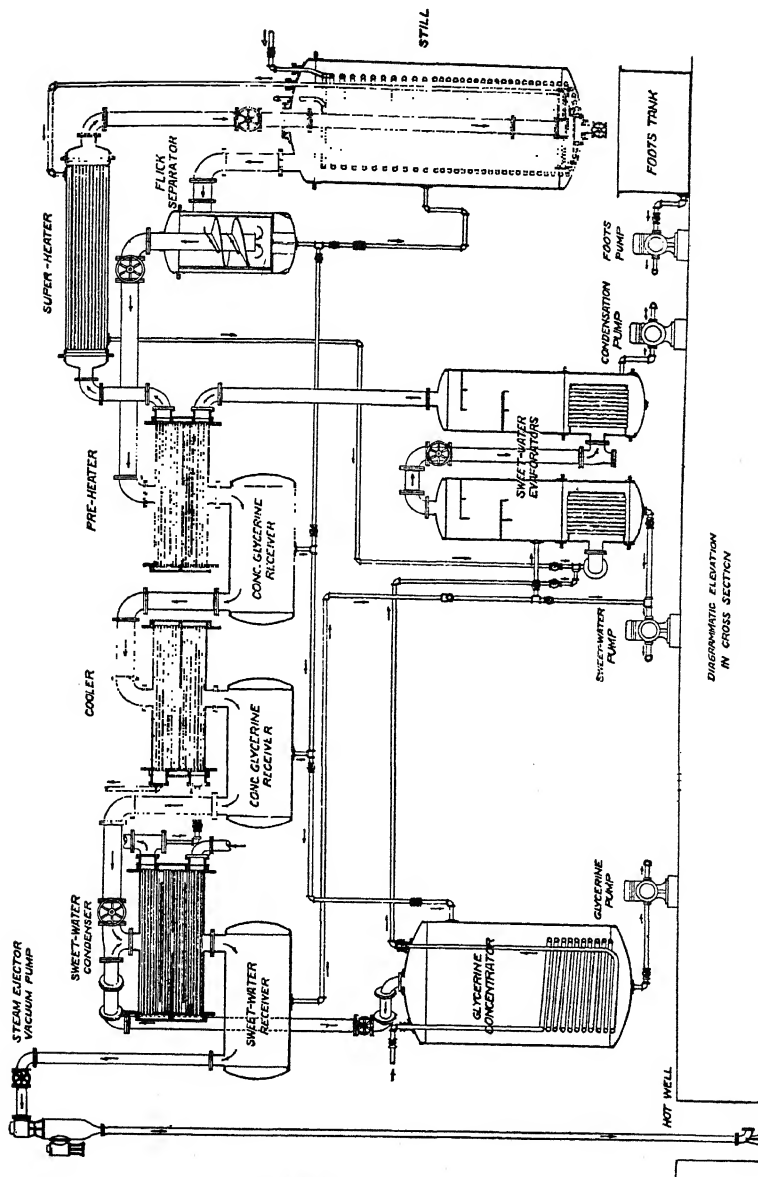
FIG. 55. Wurster and Sanger Glycerine Distillation Plant.

in general the closed system now gives a very high grade distilled glycerol.

*The Still.* — Figure 55 shows a diagramatic elevation in cross section of the newest Wurster and Sanger glycerol distillation plant. The equipment consists of a steel tank still fitted with pressure steam coils. These coils are placed closer together in the lower section of the still as they are the source of much of the heat used in the distillation. Nearer the top of the still the coils are spread out more as their value here is only to keep the glycerol-water vapors at high temperature to avoid condensation of any glycerol back into the still. For this reason, the coils should extend right to the top of the still. Leading into the still is a large vapor pipe which extends down into the liquid and has at its lower end, a cross which is perforated with many holes for the better distribution of the live steam. At the bottom of the still is a short nipple with gate valve for cleaning out foots.

*Steam Pressure.* — In the Wurster-Sanger still the coil is continuous. Steam at 175 to 225 pounds pressure enters the coil and the exhaust steam from the coil is used to heat the superheater. This system is valuable only when high pressure steam is used, as the sensible heat available for distillation is removed in giving heat for the distillation and in the upper part of the coils, the steam is no hotter than the vapors going out of the still. The vapors leaving the still pass through a Flick entrainment separator (Fig. 56), where entrained solids, high boiling volatile impurities and a small amount of the glycerol separate from the vapors and are returned to the still. The hot vapors then pass through a tubular preheater, on the outside of the tubes, where some glycerol is condensed and a considerable amount of the sensible and latent heat is reused in preheating the steam used as live steam in the still. Here the considerable portion of the glycerol which has been condensed is separated from the steam and passes into the concentrated glycerol receiver. This glycerol is of high strength as the temperatures are much above the boiling point of water.

*Condensers.* — The partially stripped glycerol vapors pass on to a second tubular condenser in which hot water passes through the tubes, the weak glycerol vapors passing on the outside of the tubes. Most of the glycerol remaining in the vapors together with a small amount of steam condenses here, giving a lower concentration of glycerol in the condensate than that from the

SECTION A-A
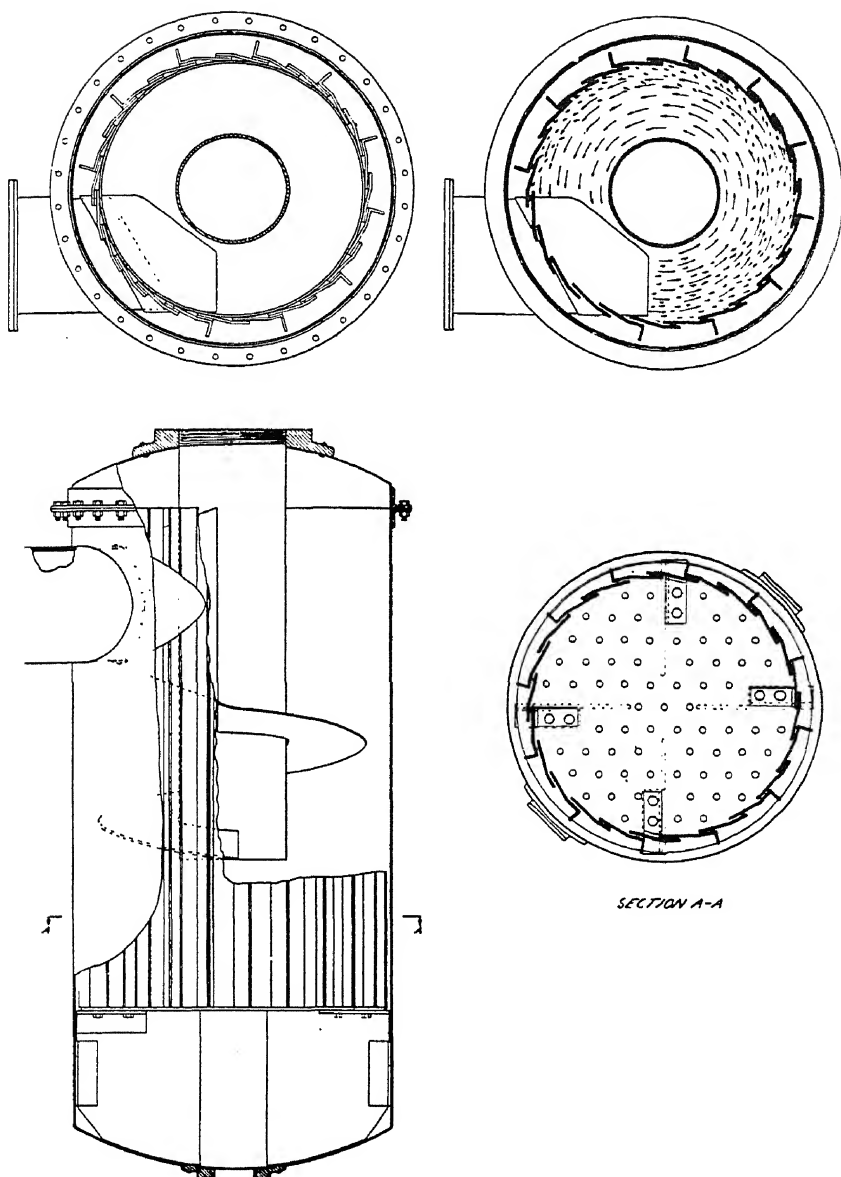
FIG. 56.   Flick Centrifugal Catchall and Entrainment Separator.
Patent applied for, Wurster and Sanger, Inc.

preheater.   The remaining vapors now pass to a final condenser in which cold water passes through the tubes so that the vapors passing on the outside of the tubes are completely condensed. This gives a low percentage glycerol sweet water.   From the receiving tank for the sweet waters, the non-condensable gases pass on to a steam ejector vacuum pump and out of the system.

*Sweet-Water Evaporators.* — The sweet waters are fed from the receiving tank to a sweet-water evaporator where the water is evaporated and the steam vapors generated pass on to the second sweet-water evaporator which, however, is fed with pure water instead of sweet water.   The vapors coming from the first sweet-water evaporator, which is under a higher pressure than the second evaporator, heat the pure water and the pure steam produced, passes from this evaporator through the preheater tubes, then through the superheater tubes to the open cross in the glycerol still.   By the introduction of the second sweet water evaporator, the main fault to be found with the earlier closed systems of glycerol distillation, that is the accumulation of low boiling volatile impurities in the system is avoided as these pass out of the system through the heating unit of the second evaporator.   On account of this improvement, it is now possible to make water white glycerol from saponification crudes in a single distillation.

*Super Heaters.* — The high pressure steam coming from the coils in the glycerol still goes to the superheater where they superheat the steam coming from the second sweet-water evaporator.   This superheated steam is at the same time expanded under decreasing pressure so that it enters the still through the " cross " as superheated expanded steam.   In this way, the closed system has adopted the valuable idea of Van Ruymbeke in using expanded superheated steam which has all the heat value of pressure steam and is readily controllable both as to temperature and amount.

Part of the steam used in the coils of the still is by-passed to the glycerol concentrator where it is used to evaporate the glycerol, coming from the two strong glycerol receivers, to a concentration of about 99 per cent.

The concentrated sweet water from the first sweet-water evaporator is redistilled along with the regular crude being used.

*Operation.* — In the operation of the glycerol still, the vacuum pump is started, a charge of crude is drawn into the still, filling it

about one-third full, steam is turned into the coils of the still and a charge of water is drawn into both sweet-water evaporators. The water present in the crude charge in the still boils off and the charge gradually is heated to about 350° F. The pure water vapors from the second evaporator are superheated and pass into the glycerol in the still through the perforated cross and the glycerol itself starts to boil. In about two hours the entire system is brought up to proper temperature. All of the condensates from the preheater and cooler are returned to the still during this period. As soon as temperatures are up so that the vapors leaving the still and those entering the preheater are about 350° F. the glycerol condensed from the preheater and coolers is collected in their receiving tanks, and, as these tanks fill up, their contents are run to the concentrator.

*The Foots.* — The time of a complete distillation depends on the kind of crude, the size of the still, and the rate of distillation. Average soap lye crudes contain about 10 per cent of salts. With such a crude and a distillation rate of 500 pounds of finished glycerol per hour, a run will take about 44 hours before it is necessary to stop the feed. The material, or foots, present in the still at this point contains considerable glycerol. If the output of the glycerol refinery is fairly large in amount, it usually pays to recover glycerol from the foots. In this case, the foots are not run to dryness. The steam is shut off and vacuum released when the foots still show about 20 to 25 per cent glycerol. In this way there is only a very small production of decomposition products of glycerol such as acrolein and socalled polymerized glycerol. The glycerol present in the foots, as well as the salts, can, by proper chemical and mechanical treatment, be largely recovered. If a foots recovery system is not operated, then the foots are distilled to " dryness," that is, until the glycerol present no longer distils over and there is a sudden rise in temperature of the vapors leaving the still, due to the free passage of the superheated steam through the foots. The foots are discharged hot to the sewer and their value both for glycerol and salts is lost. The loss of glycerol by this procedure amounts to about 2 per cent of the total glycerol. The loss through the production of acrolein with wet foots is about one-half per cent, with dry foots about three-quarters per cent. The total recovery of glycerol with dry foots is about 97 per cent, with wet foots and the foots recovery system to about 98.5 to 99.3 per cent.

After discharge of the foots, the still is washed and the contents of the receiving tanks are drawn off to the concentrator, and the system is ready for starting a new distillation.

From 4 to 6 hours is required for the cleaning and starting of operations and to bring the system back to proper working temperatures. It is possible to increase the average distillation period of a soap lye crude distillation to several times its present length by adding to the bottom of the still a secondary foots receiving tank to which most of the wet foots, but not all, would be discharged. Steam would be cut off from the coils to allow the still to cool somewhat and then fresh crude run into the still very carefully on top of the small residue of foots left in the still to avoid too sudden a production of vapors, due to the water present in the crude glycerol.

*Wood Multiple Effect System.* — There are several other systems for the distillation of glycerol, such as the Wood multiple effect in which the glycerol is distilled by a flash method in a battery of three to six stills arranged in series, the undistilled glycerol passing from one still to the next, the successive stills being under slightly decreasing pressures. The undistilled glycerol from a still is reheated in a tubular heat exchanger, which is heated by live steam and thus the temperature of the glycerol to be distilled is maintained. This system is very expensive with regard to construction, because of its complexity and number of units. Great economy in steam consumption is claimed, but it is doubtful if it is as efficient as the new closed system which·uses three pounds of steam per pound of glycerol recovered from average 80 per cent soap lye crudes, and two and one-half pounds per pound of glycerol recovered from saponification crudes.[13]

*Costs.* — The cost of distilling 80 per cent soap lye crudes to dynamite grade glycerol will vary somewhat with local conditions, covering the cost of steam, labor, etc. The factors entering into the final cost which must be ascertained are as follows:

Cost of 80 per cent soap lye crude per pound.
Pounds of steam used per pound of finished glycerol.
Cost of steam per pound.
Amount and cost of water for condensers, etc.

[12] For description of other stills, see "Glycerol and the Glycols," J. W. Lawrie, Chemical Catalog Co., 1928.

If electrically driven vacuum pump is used, then its power con-
sumption and cost for power.

Yield of finished glycerol 100 per cent based on input of crude,
basis 100 per cent.

Labor costs per pound finished glycerol.

Cost for foremen and supervisors.

Amount and cost of decolorizing carbon used.

Repairs, repairs materials and labor for same.

Depreciation (figured as a per cent of the original cost as an
annual charge against final replacement of equipment.

Taxes.

Insurance on equipment.

Insurance on men such as employees' liability.

Ground rent on space occupied by the refinery and its adjuncts.

Interest on investment in equipment, buildings, working capital,
etc.

Overhead in buying raw materials, selling finished product,
clerks, manager, etc.

Chemical control. Analyses of raw materials and finished prod-
uct.

### RECOVERY OF FATTY ACIDS BY STEAM DISTILLATION

Low grade fats and oils are often treated for the recovery of
fatty acids. The increasing use of high grade fats and oils for
food purposes has made more or less essential the use of lower
grade fats and oils in the soap industry. Very often these low
grade materials are so impure that they cannot be used as such.
It is first necessary to treat these materials to produce crude fatty
acids. These crude fatty acids are usually produced from the
lower grade fats and oils by acid or alkali hydrolysis, which
should be as complete as possible so as to leave only a small
amount of free fats along with the fatty acids.

The impure fatty acids separate from the glycerol-water, which
is withdrawn. The acids must be thoroughly washed to remove
lime or sulphuric acid used in the hydrolysis.

**Drying.** — The crude fatty acids are them pumped to a drying
and feeding tank. In this tank, they are heated by steam in
coils to a temperature of 220° F. (105° C.), using air agitation.
At this temperature, and with efficient agitation, the fatty acids
are thoroughly dried. The need for thorough drying is that any

moisture entering the hot still, which is at a temperature of 425 to 550° F., would cause a sudden formation of steam which might make the still prime and cause some of the crude acids from the still to pass to the condensers, thus giving an impure distilled stock.

**Still.** — In Fig. 57, which is a diagrammatic sketch of a Wurster-Sanger fatty acid distillation plant, the still $A$ is constructed of
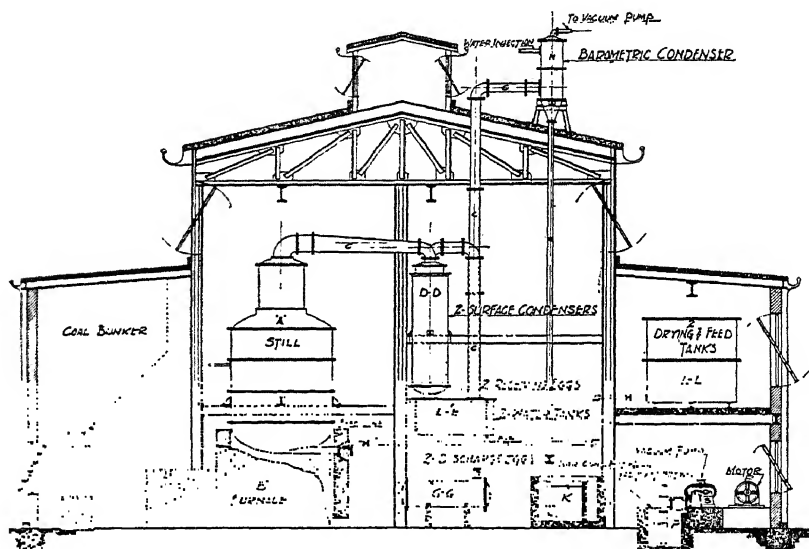


Fig. 57. Fatty Acid Distillation Unit, Wurster and Sanger.

cast iron in sections. The bottom section is cast in one piece and is made thicker than the other sections, because this section is exposed to the highest temperature, is longer in contact with the fatty acids, and wears more because of these conditions. It is, therefore, made so that it can be readily replaced with a new section. For this purpose, the still is hung from lugs on the section just above the bottom one. The average life of a bottom section is about five years, of the upper sections much longer. Owing to the high temperatures required in the distillation of fatty acids (up to 550° F.) direct heating is largely used. It is possible, however, with the recent development of high temperature resisting oils, to use an oil heating system in which these

oils are circulated through coils inside of the still, to avoid the use of direct heat. Some of these oils will stand temperatures of over 600° F. continuously, with but little decomposition. The use of such a system of heating eliminates some of the decomposition of fatty acids which takes place with direct heating from local overheating. This local overheating increases the tar yield and gives a poorer colored distillate, which has also a less desirable odor.

**Condensers.** — Connected to the vapor outlet of the still are two condensers, *D–D*; constructed with copper dome, tubes and bottom section. The water jacket is made of steel. These condensers are cooled with water at a temperature of 100 to 110° F. so that the fatty acid vapors will condense to a liquid, but will not solidify. With high-melting fatty acids, such as stearic, it is necessary to keep the condensers at even higher temperatures to prevent the solidifying of the fatty acids in the tubes.

The condensers are connected each to a receiving tank or egg for holding the distillates. These eggs are set in water pans which have steam coils so that the fatty acids can be kept liquid. The steam vapors used in the distillation, and the non-condensable gases, pass from the receiving tanks to a barometric condenser, which is in turn connected to a vacuum pump of either the mechanical or steam jet type. Below the receiving tanks are the discharge tanks. When a receiving tank is almost full, the contents are let down into the discharge tanks *G.G.* from which the fatty acids can be removed by pumping to storage tanks.

**Operation.** — In operating a fatty acid distillation plant, with a still of 9 feet diameter by 17 feet deep, provided with 1000 square feet of copper condensing surface in the two condensers, a charge of 15,000 pounds of hot dry fatty acids is run into the still from the feed box. The gauge glass is so placed on the still that this volume of acids will show about the center of the glass and this level is maintained as closely as possible throughout the distillation run, until the feed is stopped and the tars are being run down. The fire is now started under the still, or hot oil is circulated through the heating coils. The superheater for steam is fired and this steam is by-passed until it is up to temperature.

The steam going to the superheater is usually under a pressure of 15 to 20 pounds. The steam valves going to the superheater are all wide open, the regulation of the amount of steam passing into the still being controlled by the main steam valve next to the still. It is well to have two valves in the steam line coming from the superheater to the still to provide for any emergency, the first valve being wide open, the final valve being used for control purposes. This valve is now set so that the steam entering the still is practically at atmospheric pressure or zero gauge pressure. A small stream of water is turned into the barometric condenser, and warm water into the surface condensers and water pans containing the receiving eggs.

*Temperatures.* — The temperature of the still is brought to 450° F. and the temperature of the superheated steam to 550° F. as rapidly as possible, when it is turned into the still. While the temperatures in the system are rising, some of the steam will condense in the surface condensers and pass into the receiving eggs from which the condensate should be removed by pumping or blowing. The fatty acids will start to distill over at a temperature of 410° to 425° F. As the system heats up, the rate of distillation will increase and it will be necessary to control the temperatures of the condensers so that the water discharging from the condensers will have a temperature of about 140° F., the water entering having a temperature of 100 to 110° F. The water entering the barometric condenser should be so regulated as to have a temperature of 115 to 120° F. on leaving. It has been found in plant practice that the cooling water discharged from the first surface condenser should be at a temperature of 160°, and from the second at a temperature of about 130° F.

*Feed.* — As the fatty acids distill over, the level in the still is maintained by feeding the dry crude fatty acid from the feed tank. If, at any time, too great a feed has been used, so that the feed must be cut off, then the feed line should be blown out with steam back to the feed tank so as to avoid freezing of fatty acids in the line, or the line itself should be steam jacketed so that such a freeze-up is avoidable. In general, the feed tanks are located high enough so that the still may be fed by gravity and suction due to the vacuum in the still.

*Condenser Temperature.* — The temperature of the water in the condensers is regulated according to the kind of fatty acids being distilled. Care must be taken always that this temperature is

higher than the melting point of the fatty acids so that the tubes of the condensers cannot become clogged with solidified fatty acids. The water discharge from the barometric column is held as low as possible, consistent with obtaining and maintaining a high vacuum in the still.

*Steam and Fuel.* — On the average, usng direct fired stills, one-half pound of steam is required per pound of fatty acid. The rate of distillation with the size equipment described, should be from 1500 to 2000 pounds per hour. The coal requirements under careful operating conditions with a direct fired still are about 100 pounds per hour including the superheating of the steam.

*Capacity.* — The total time of a run depends on the quality of the crude fatty acids and the rate of distillation. With black fatty acids, 50,000 to 125,000 pounds can be fed to the still before it is necessary to run down to pitch. With fatty acids obtained from cotton seed foots, from 50,000 to 60,000 pounds will be distilled in a run, whereas with fatty acids recovered from garbage grease or low grade animal fats, from which the pitch yield is low, a run will take from 60,000 to 125,000 pounds of crude.

*Pitch.* — When the distillate begins to darken toward the end of a run, and the odor is bad, then the feed should be shut off, and the charge in the still run down to pitch. Samples of the pitch are taken at frequent intervals. When the pitch will pull out in long threads, and is fairly dry when worked in the fingers, then the run is completed. With tar from acidified cotton seed foots, still temperatures as high at 600° F. must be reached before drawing off the pitch. As the samples of pitch taken through the vacuum sampler valve show that the run is almost completed, no more coal is added and the bed of fuel is broken up so as to burn freely.

As soon as the pitch is ready for discharge, the fire bed is withdrawn or the oil or gas fuels are shut off, the valve on the vacuum line to the barometric condenser is closed, and steam is turned on to the ejector on the tank. The vacuum on the still starts to drop. When the pressure on the still is at zero gauge reading, and a vacuum of about 20 inches has been produced in the pitch receiving tank, the superheated steam to the still is shut off. Steam is kept passing through the superheater either to the atmosphere or to another still. The tar cock is now opened and

the pitch from the still passes to the tar box.    When the still is empty and the vaccum on the still and tar box is equalized through the discharge line, the tar cock next to the tar box is closed.    The tar line from the still is now opened to discharge into an open barrel or drum, and steam from the superheater is turned into the still for 10 to 15 minutes.

If the pitch has become so hard that it will not discharge from the stills, a small charge of crude fatty acids is added and the distillation is continued, but is not carried quite as far as previously.    The tars are then discharged in the regular way.

The tar from the tar tank is run into barrels or drums while still at a temperature of 300 to 350° F.    The tar tank is provided with a small furnace so that a fire can be made to take the chill out of the brick setting and the tank.    Only a small fire should be made and care should be taken as the gases given off by the hot tar are inflammable.    On account of this, a red hot bar should never be used up to open the passage way of the discharge cock.    A warm bar may be used.

*Redistillation.* — In redistilling once distilled fatty acids, the same procedure is used as for crude fatty acids, but owing to the smaller amount of tar the time of the run is much longer and the quality of the distilled acids is better.    Instead of running the tars down to final pitch, they can be discharged and added to the crude fatty acid still.    In this way, no hard pitches are left in the still and the color of the second distilled fatty acids is kept to a higher standard.

*Yield.* — The yields of once distilled fatty acids varies considereably with the kind of crude used.    The less neutral oils or fats, left in the crudes, the higher is the yield of distilled fatty acids.    The yields of recovered fatty acids may, therefore, vary from 70 to 95 per cent with pitch of 4 to 25 per cent.    There is always a loss of several per cent, due to decomposition and the production of gases.    The yield of twice distilled fatty acids likewise varies with the type of crude.    From acid treated cotton seed foots, the yield of double distilled acids is about 85 per cent of the weight of crude acids, and 12 per cent of pitch.    Garbage grease crude acids give a yield of about 90 per cent of twice distilled acids and 6 per cent tar.

There are no color standards for distilled fatty acids which have been accepted throughout the trade.    In general, distilled fatty acids are sold on the basis of representative samples.    For

comparative purposes, the Lovibond Tintometer color readings are accepted, using 1 inch glass cells. Once distilled fatty acids acceptable from the color standpoint will have a color of about 35 yellow, 7 red, and for twice distilled, 35 yellow, 4 red.

Wurster [14] gives a cost estimate for the production of twice distilled fatty acids operating two stills at $0.65 per 100 pounds. These costs will vary according to local conditions, labor, steam, etc.

### LABORATORY DISTILLATION AND FRACTIONATION EQUIPMENT

There are numerous types of laboratory distillation equipment, described and illustrated in various journals and books. Many of these are complicated, difficult to construct, delicate to handle and unavailable to the average laboratory. To avoid these difficulties, the author has designed a simple still body and column (see Figs. 58 and 59), which can be used for distillations with steam, or inert gases, at atmospheric or reduced pressures. It is possible to construct a still for pressure distillation using materials of construction which will withstand the pressures desired. The still body consists of a round bottom flask fitted with three openings, one for a thermometer, one for the steam and feed inlets, and a large center opening for the fractionating tube or column.

**Bumping.** — To prevent excessive bumping during vacuum distillations, a piece of metal gauze is rolled so as to pass through the large opening in the distilling flask, and is then spread out as much as possible. It is held upright by two pieces of wire which reach up into the neck of the flask. This device has been found to be very satisfactory, even under the highest vacuums. Direct heating with resistance wires in the liquid has also been found very satisfactory, but is not applicable to liquids which are inflammable, or which are good conductors of electricity unless the wires are properly insulated.

**Column.** — The type of column to be used is dependent on the liquid being distilled and fractionated. If the liquid is a high boiler, or contains high boilers, as well as low boilers, a relatively wide tube must be used, for low boilers a narrower tube may be

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[14] Chem. & Met. Eng., 25, 3, 1921.

BRUHL RECEIVER FOR COLLECTING
SEPARATE FRACTIONS

LABORATORY
FRACTIONATING COLUMN
AND EQUIPMENT
FOR HIGH BOILING LIQUIDS

Use 18 Gauge Cu. Wire
Wind long Spiral
on ⅛" Rod & cut
into ¼" Lengths

COLUMN PACKING

SET-UP FOR
WATER DETERMINATION
IN
GLYCEROL & GLYCOL

Condenser

Adapter

To
Vacuum
Pump

Receiver

Freezing
Mixture

CaCl₂ Tube

Condenser

Drain to
be Flush
with
Stopper

1000 cc. Pyrex
3 Neck Distilling
Flask

Roll of
Copper Gauze
for Anti-Bump

FIG. 58.  Laboratory Fractionating Column and Equipment for High
Boiling Liquids.

LABORATORY
FRACTIONATING COLUMN
FOR LOW BOILING
LIQUIDS

BRUHL
RECEIVER

Detail of Column Packing

FIG. 59. Laboratory Fractionating Column for Low Boiling Liquids.

used. If the material to be distilled is small in quantity, then a short and narrow tube is used.

**Column Filling.** — The fractionation column is filled with spirals of wire, iron, copper, monel metal or any metal which does not affect the material being distilled. A close-wound spiral coil of about 20 gauge wire is made, which will be of such outside coil diameter that it will just fit snugly into the column. This coil is then stretched so that the rings of wire are about 1/16 inch apart. The coil is placed in the column reaching from just below the vapor outlet, down to within about 2 inches from the bottom. A second spiral is now made such that it will fit inside the outer coil not too snugly. The rings are again about 1/16 inch apart and it is best to wind this coil in the direction opposite to the winding of the first coil. If the column is large enough, then a third coil is prepared in the same manner as the first coil. The final center coil is made by twisting two pieces of the wire around each other. The friction of the rings of the outer coil against the wall of the glass tube is usually sufficient to hold it in place, and the other coils are anchored at the top of this coil by spreading their top rings above the top ring of the large coil.

**Distilling Capacity.** — The value of this type of column filler is that it leaves a very large amount of open space in the column, about 70 to 80 per cent, but it presents an extremely large surface for vapor contact. This contact surface is further very largely increased by the formation of films of condensate between the rings of each coil and from coil to coil. The distilling capacity of such a filled column has been found to be several times that of a cut glass filled column, or of a bead filled column, the fractional cuts can be made much closer and the holdback in the column is less than for either of these other filled columns. The wire coils may be easily removed for special cleaning, and replaced.

**Dephlegmator.** — The column is filed to an angle of about 45° at the bottom. This is readily accomplished in the laboratory, using a piece of iron wire gauze and drawing it against one side of the edge of the glass tube. A little practice will show the best way of producing this pointed end. With such an end, the column has much less tendency to become filled with liquid than the straight edged column or the column with a drawn out tip.

About 12 inches from the top of the column a dephlegmator jacket is either sealed to the tube or held in place by a cork or rubber stopper. An outlet for water is fitted at the bottom of the dephlegmator. Water in controlled amount flows into the top of the dephlegmator section. The level of the water in this section is controlled by the height of the outlet $F$ which is a glass tee connected to the lower outlet of the dephlegmator by a rubber tube. The overflow of water passes through the side arm of the tee to the sink. A thermometer is fitted into the upper arm of the tee. With a thermometer in the dephlegmator and with a known volume of water flowing through the dephlegmator, the heat values, etc., of the distillate passing over can be determined approximately.

At the top of the column is a vapor outlet and a thermometer well so that the temperature of the vapor passing from the column can be accurately taken. Over the main body of the column a glass jacket is fitted to prevent uneven cooling from air currents. When high temperature boiling substances are being distilled this jacket may be heated with a stream of hot vapors, or gases, or liquids, to decrease the wall condensation in the column. In such a case, cold water is not used in the dephlegmator, but water or other liquid may be heated and passed through the dephlegmator.

**Applications.** — This still body and column have been found of great value in the fractionation of many solutions or mixtures of materials, such as butyl alcohol, ethyl alcohol, acetone and water, ethyl alcohol and water, glycerol and trimethylene glycol, glycerol and ethylene-glycol, etc., giving separations in most cases as close as 1/10 of one per cent, relatively pure fractions and sharp cuts.

For steam distillations, the equipment shown in Fig. 54 has been found to be of rather general application. Steam is either taken from a low pressure line or is produced in a flask as shown in the diagram. It may be superheated and the temperature controlled by regulation of the superheater. The superheater may be just a metal tube heated with a flame or the tube protected from the direct flame with a piece of iron pipe. A more easily controlled and more satisfactory method of superheating the steam is to use a metal tube surrounded by a small resistance wire wound heater controlled through a rheostat. The feed to

the still is made either through the opening in the flask for the steam inlet, or it may be made through the center opening in the still head or catchall. In this latter case, the feed pipe acts as a partial dephlegmator or condenser, giving more reflux and, at the same time, the feed is heated approximately to the temperature of the out-going vapors.

The still head is made from a Kjeldahl flask of about 800 cc. capacity. The neck is cut off and filed to an angle of about 45°. In the bulb are three openings, one for a thermometer, one for a feed or steam inlet, and the third for vapor outlet. The still head may be covered with asbestos or fibre insulation to prevent undue refluxing for high boiling materials. The large neck permits rapid distillation without plugging, and the bulb head serves as an entrainment and foam separator. For certain materials, it has been found useful to insert a coarse wire gauze cone where the bulb and neck join, and partially to fill the bulb with either cut glass or spiral wire fillers to assist in preventing entrained matter going over to the condensers.

**Air Condensers.** — For glycerol, and other high boiling liquids, two air condensers have been found to be useful. The first air condenser will contain most of the high boiling material. Steam, together with any other low boiling material, and a small fraction of the high boiling liquid vapors, will pass to the second air condenser. The outlet from this second air condenser is made in the form of a scrubber filled with small wire spirals or cut glass. This scrubber removes the last traces of the high boiling material, allowing steam and any low boiling material to pass on to the final cold water condenser.

**Wire Spirals.** — The method of making the small wire spirals is shown in Figs. 58, 59, and 60. Light wire, such as 18 gauge copper, or any metal wire which will not react with the material being fractionated or distilled, may be used. Iron wire, however, tends to rust very readily. A rod or tube is chosen such that when wound it will slip into a large tube easily. The larger tube is taken such that it will give a spiral of the desired diameter. In this larger tube, a notch is cut at one end. The wire is wound on the small rod making about eight turns, each one sixteenth of an inch apart. The rod with the spiral is inserted in the larger tube with the free wire at the notch end. The free wire is bent into the notch, and the remainder of the wire is wound in the

opposite direction away from the notch, each spiral being one-sixteenth inch apart. About eight spirals are made, the excess wire is cut and the finished spiral is removed. These fillers, made
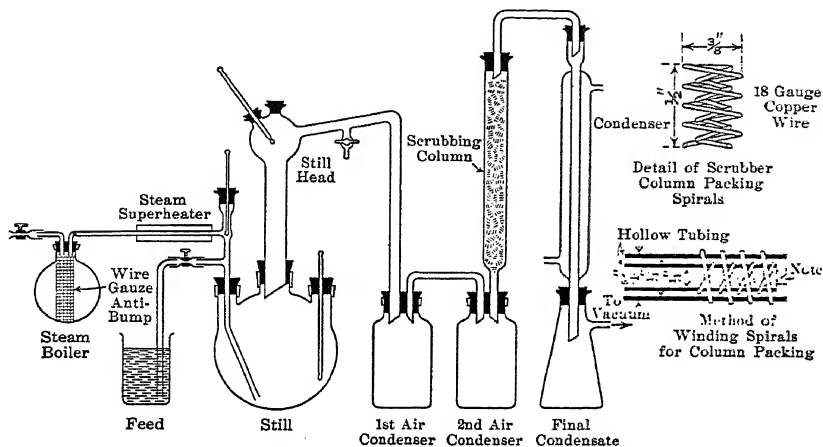


FIG. 60.  Laboratory Still Arranged for Steam Distillation with Scrubbing Column.

after the manner of Bregeat fillers, have been found to be much better in almost every way than cut glass or glass bead fillers, having greater capacities, more efficient scrubbing and less hold back in the column.

In distilling glycerol, as an example, the vapors leaving a two foot by two inch scrubber have contained only 0.0017 per cent glycerol, whereas, without the scrubber we have had as much as 30 per cent of the glycerol passing to the final condenser. The scrubber serves as a very efficient entrainment separator and under suitable conditions of reflux gives a definite separation of high and low boiling liquids.

### Problems

19. On distilling a mixture of benzene and ethyl alcohol at normal pressure (760 mm.) we have a constant boiling mixture at 68.25° C. The vapor pressures of benzene and ethyl alcohol at this temperature are approximately 425 mm. and 335 mm. What is the percentage of each material in the vapor?

20. The constant boiling temperature of a mixture of water and butyl alcohol is 92° C. The vapor pressure of water at 92° C. is 567 mm. and of butyl alcohol 193 mm. What are the proportions by weight of each substance in the vapors?

21. Butyl alcohol is distilled with steam at a pressure of 75.7 mm. Hg. The

temperature of the distillation is 40.6° C.   What are the partial pressures of each component?   What are the proportions by weight of each component in the vapors?

22. By Trouton's law determine the latent heat of vaporization in calories per gram at the boiling points of water, ethyl alcohol, ethyl acetate, ammonia.

23. In distilling aniline with steam, the boiling point of the mixture is 98° C. at 760 mm.   How much steam is required per pound of aniline distilled?

24. The gauge on a still shows a pressure of 44.1 pounds.   The temperature is 141° C.   The still contains water and an organic liquid.   What is the partial pressure of the organic liquid?   What is the per cent by weight of the organic liquid in the distillate if the organic liquid is benzaldehyde?

# CHAPTER VI

## DRY DISTILLATION AND BY-PRODUCT RECOVERY

F. W. SPERR, Jr., B.A., and J. F. BYRNE, B.S., M.S.

Dry distillation or destructive distillation, as it is sometimes called, is the process whereby a solid material is decomposed by heat in the absence of air and the volatile products of the reaction are distilled off and recovered. A by-product is a material which is produced incidentally in the manufacture of a specific commodity (or primary product) and which possesses a market value of its own.

**Products.** — Coal and wood are the raw materials most generally treated in the large-scale industries by dry distillation, although small tonnages of bones are also dry distilled. In the distillation of coal, coke is the primary product and gas, tar, ammonia, and light oils are the principal by-products. Charcoal is the primary product of wood distillation and alcohols, turpentine, resins, and other oils and chemicals are recovered. From bones, bone black is produced which is used as a pigment and as a decolorizing agent. Tar containing quinoline and pyridine is recovered and also a small amount of gas which is consumed in the process. The distillation of oil shales, although not of substantial commercial importance at present, may attain such importance in future years as petroleum resources become depleted.

**By-Products.** — The line of demarcation between principal products and by-products is neither sharp nor rigid. Developments in technical processes and changes in economic conditions cause the various products to change in relative importance, so that what were by-products or even waste products in one decade may be primary products the next. In the manufac-

ture of coke in beehive ovens, the tar and gas are wasted, coke being the only product. In modern plants, gas, tar, and ammonia, in addition to the coke, are recovered and the success of the industry depends upon the proper marketing of each of these products.

### By-Product Coking Industry

The by-product coking industry is by far the most important of the processes employing dry distillation. It utilizes numerous unit processes of chemical engineering both in the distillation and in the recovery of the products. Because of the magnitude of this industry and because of the diversity of processes employed, it will be described as an illustration of dry distillation and by-product recovery.

By-product coking is perhaps the outstanding case wherein by-products have completely revolutionized both the engineering and economic aspects of an industry of years' standing. In most industries, the recovery of by-products entailed simply an addition to the existing process. The basic principles remained unchanged, the fundamental equipment, unaltered. The coking industry, however, underwent a different experience. Existing plants were found to be entirely incapable of adaptation to by-product recovery and had to be replaced in entirety. Practically the only points of similarity between the beehive coke process and the by-product process are the raw material, coal, and the nal primary product, coke.

Despite the magnitude of this change, by-product coking has risen within only thirty years to an industry which employs the highest type of engineering ingenuity, which manufactures over 90 per cent of the total coke produced in the United States, and whose annual sales total over $400,000,000.

**Coal — Its Origin and Nature.**[1, 2] — Before discussing the engineering aspects of the coking industry, a brief mention of its principal raw material — coal — is appropriate. Coal is essentially the metamorphosed remains of prehistoric forests. During the Carboniferous Period, climatic conditions existed which produced an extremely luxuriant vegetation, the debris of which settled into swamps, analagous to the peat bogs of today. During succeeding ages these swamps were covered with a series of geologic deposits and were subjected to the influence of dias-

trophic movements, the results of which are the coal fields of today.  Of the various ranks of coal — lignite, sub-bituminous, bituminous, semi-bituminous, and anthracite — the coking industry is concerned primarily with bituminous and semi-bituminous coals, with a minor interest in sub-bituminous.  The exact classification of coal is still a moot question, but the following may be taken as a general range of analysis:

| | Moisture | Per Cent of Combustible | | B.t.u./lb. (ash free) |
|---|---|---|---|---|
| | | Fixed Carbon | Volatile Matter | |
| Sub-bituminous.............. | 11–23 | 42–47 | 34–41 | 9,720–12,880 |
| Bituminous.................. | 3–5 | 54–65 | 32–41 | 13,880–15,160 |
| Semi-bituminous............. | 3–5 | 75–83 | 11–22 | 15,360–15,480 |

Coal from the same mine may vary both in analysis and in coking properties.  Furthermore, an analysis alone is of little value as a criterion of the quality of coke and the yield of by-products that can be obtained from a given coal.  These matters can be determined only by actual tests under conditions analogous to those in a commercial coke oven.

The highly complex chemical compounds of which coal is composed, are, like most compounds in vegetable and animal life, unstable when subjected to high temperatures in the absence of air.  They decompose to form gases and a carbonized solid residue.  When a coking coal is heated in the absence of air, it fuses or melts, gases are evolved, and the melted mass solidifies while the gases are still coming off, into a coherent mass of cellular structure, composed of carbon plus the ash which was originally present in the coal.  This solidified residue is coke and the vapors distilled in the process contain the by-products.

**Historical.**[3] — Coke was manufactured by the Chinese over 2000 years ago.  It was used in the arts and to a slight extent for domestic purposes in the middle ages.  The first record of coke produced in an oven is an English patent of 1620, but there was little practical development during the next hundred years.  During the 18th century, several patents were granted for manufacturing coke in beehive ovens and also for the production of tar, pitch, and oils from coal.

The gas industry, producing coke as a by-product, was established on a commercial scale in London in 1812 by William Murdoch. The coke produced was of inferior quality and the surplus gas not employed in heating the retorts was sold for domestic use. The gas industry and the coke industry developed along separate though parallel lines for many years. At present, however, the two industries can well be considered together, as the by-product coke oven has been proved beyond question to be the most efficient source of coal gas for city distribution.

The first coke was produced in mounds. The coal was arranged in heaps, these heaps being provided with horizontal and vertical flues filled with wood. The wood was ignited and the fire permitted to extend through the entire mass. When the gaseous matter was burned off, the heap was smothered with dust, and perhaps a small amount of water. The state of the weather had considerable influence on the time required, the average period being from five to eight days.

*Beehive Ovens.* — The next step was the beehive oven, which consists essentially of a circular, dome-like chamber lined with fire brick, provided with an opening at the top for charging the coal and for the escape of the products of combustion. A door is located at the side of the chamber, through which air for combustion is admitted and through which the coke is withdrawn when the process is completed. After the coal is charged to the oven, the side door is partially bricked up. Heat stored in the oven walls from previous charges is sufficient to raise the coal temperature to such a degree that the volatile matter is evolved, and ignites with the air above the charge. The heat thus generated causes the coking to proceed until all the gases are driven off, when the process is completed. This requires 48, 72 or 96 hours, depending primarily upon the thickness of the coal charge.

There are several modifications of the beehive oven, but they are all similar in that coke is the only product recovered, the by-products being consumed in the coking process. The intrinsic characteristics of the beehive oven render it unsuited for by-product coking. Consequently all attempts to recover by-products, while retaining the basic principles of the beehive oven, were unsuccessful. A radical change was necessary, and it was not until the externally-heated chamber oven was designed that by-product recovery became successful.

*By-Product Ovens.* — The first commercial ovens for by-product recovery were constructed by Knab, near Paris, France in 1856. These were followed by several other plants of improved design, but all suffered from the same defects, to wit, enormous loss of heat in waste flue gases, and flue temperatures too low to produce a good grade of coke.

In 1882, Hoffman applied the principle of the Siemens regenerator to the vertical-flue type oven, using two long regenerators for each battery. This greatly increased the efficiency of by-product ovens, but the results were still far from satisfactory. The accepted method of heating was to burn the gas with the preheated air in a separate combustion chamber and to pass the hot combustion gases through the heating flues. The amount of gas that could be burned was not dependent so much on the temperatures of the heating flues as on the temperatures of this combustion chamber. Consequently the rate of coking was slow and the heating of various portions of the oven walls was decidedly irregular.

Shortly after 1900, Heinrich Koppers invented ovens in which the gas was burned directly in the heating flues. The heat generated in the combustion could pass directly into the coal charge with the result that more uniform heating and a much shorter coking time were attained. Koppers also substituted for the longitudinal regenerators then in use, individual crosswise regenerators for each oven. These two improvements made possible the separate regulation of each oven with respect to its supply both of gas and of air, and also permitted accurate control of the combustion in each flue. The result was an increase in surplus gas, from 25 per cent to 30 per cent as was obtained in the older systems, to over 50 per cent, in addition to a decreased coking time. These developments, together with the Koppers direct process of ammonium sulphate manufacture so greatly improved the by-product coking operation that they may be said to mark the real beginning of the modern period of the industry.

*Growth of By-Product Coke Industry.* — The first by-product coke plant in the United States was erected in 1893 at Syracuse, N. Y., a battery of 12 Semet-Solvay ovens. Other plants followed until in 1910 there were 4078 by-product ovens, producing 17.1 per cent of the total coke produced in the United States in that year. The first plant of Koppers ovens was

installed by the U. S. Steel Corporation at Joliet, Illinois, in 1909. Since that time, the by-product coking industry has grown steadily, due both to the increased demand for coke and to the replacing of beehive coke by by-product coke.

At the close of 1930, there were 12,831 by-product ovens in the United States.[4]   These ovens produced 45,195,705 net tons of coke, or 94.2 per cent of the total coke produced in this country. They carbonized 14 per cent of the bituminous coal mined in the United States in 1930, and the resulting coke and by-products had a market value of over $400,000,000.[5]

**Description of By-Product Ovens.** — The modern by-product oven consists essentially of three main parts: (1) the coking chamber, where the carbonization of the coal occurs; (2) the heating flues, in which combustible gases are burned to furnish heat for the coking process; and (3) the regenerative chambers, in which the air or the air and gas for combustion are preheated by the waste heat which is extracted from the flue gases.   The coking chamber is rectangular in section from 20 to 42 feet in length, 6 to 13 feet in height and 12 to 22 inches in width, the dimensions depending mainly upon the requirements of the individual plants.   The ovens are constructed in batteries of from 10 to 90 ovens, in which the coking chambers alternate with the heating chambers.   Coal is charged through openings in the top of the coking chambers, and the coke is pushed from one end of the oven by a pusher or ram acting through the other end. The ovens taper slightly in width from the so-called coke side to the pusher side to facilitate the removal of the coke.   Quenching of the hot coke is generally done by spraying the coke with water after it has been pushed from the oven.

During the coking period, the ends of the ovens are closed by brick-lined doors, and the charging openings are covered by iron lids.   Connected to the top of the ovens are suitable off-takes or "standpipes" through which the volatile products are removed during the distillation.

For the most successful coke-oven operation, heat should be applied to the oven walls in such a manner that the coking of the charge of coal will be completed everywhere at the same time and at approximately the same temperature.   The application of heat must be uniform from the top to the bottom of the coal mass, and a little more heat must be applied to the coke end

than to the pusher end, because of the taper of the oven, mentioned above.   The heating of a wall of the area now used in by-product ovens, uniformly and at such a rate as to obtain short coking time, and without endangering the brick work by local overheating, is a problem that requires great ingenuity and engineering skill.

The various types of coke ovens differ in arrangement of heating flues, design of regenerators, method of heating and many details of design and construction.   The Semet-Solvay system employs horizontal heating flues, while the others use vertical flues.[6] For the purposes of this chapter, it will suffice to describe the Koppers and the Becker ovens as these are by far the predominating types in this country.

*Koppers By-Product Coke Oven.* — Figures 61 and 62 are views of a model of the Koppers by-product coke oven.[7]   The gases
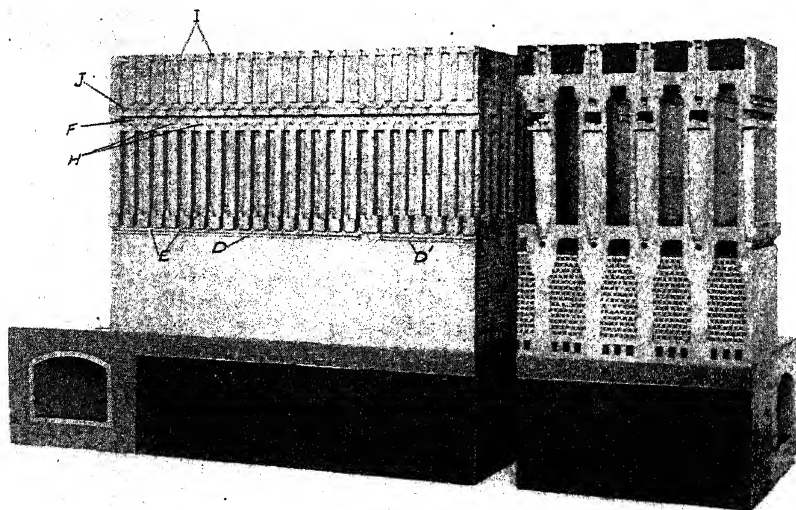


Fig. 61.   Model of a Koppers By-Product Coke Oven.

burn upward through the set of flues on one-half of the wall. Combustion gases collect in the upper horizontal flue, from which they are distributed to the flues on the other half of the same heating wall.   They pass downward through these flues and through the regenerator below, where heat is extracted from

them, into the stack flue and out to the stack. At regular in-
tervals, generally 30 minutes apart, the flow of gases is reversed,
combustion occurring in the flues previously used for the down
passage of gas.
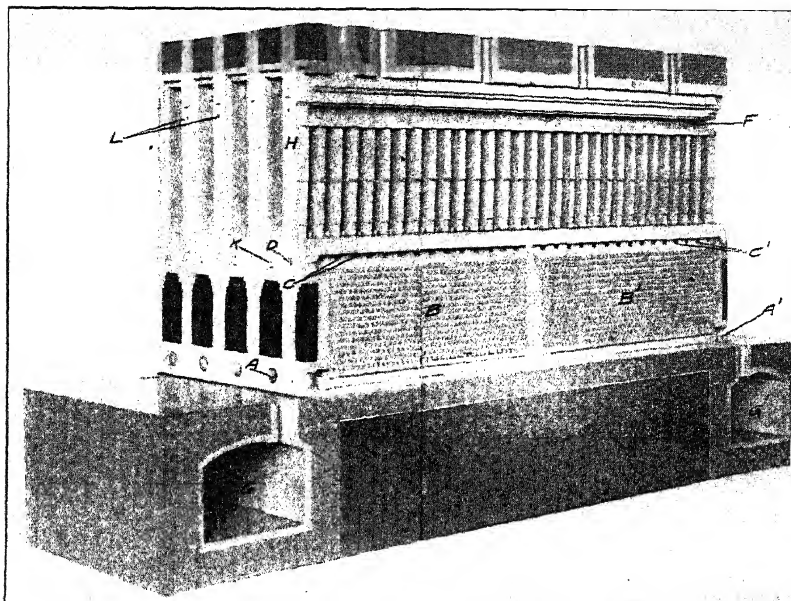


FIG. 62.   Model of a Koppers By-Product Coke Oven

When coke-oven gas is used for heating the ovens, only the
air for combustion is preheated in the regenerators, but when
producer gas is used, both the gas and air are preheated in
separate sections of the regenerators and are mixed at the base
of the combustion flue. At the reversal, the regenerator previ-
ously heated by the combustion gases is now used to preheat the
incoming gas, or air and gas.

Referring to Figs. 61 and 62, at the period when the gas is burn-
ing in the flues on the left-hand side of the block of ovens and coke-
oven gas is being used: The air for combustion passes through a
casting fitted into the opening $A$, and is distributed through the
regenerator $B$ which has been heated during the previous period.
Thence the air passes into the several airports $C$, communicating
with the vertical flues. Gas is admitted through a burner flue

*D*, and passes upward through the nozzles *E*, into the flues. Combustion takes place upward through the flues and into the horizontal flue *F*. The products of combustion pass down the vertical flues in the opposite half of the wall and escape into the opposite regenerators *B′*, through the ports *C′*. Here they impart most of their heat to the checker work and finally emerge into the stack flue *G′*, through a casting (not shown) which connects *G′* to *A′*. At regular intervals, the flow of gases is automatically reversed.

Control of draft is effected individually for each flue by manipulation of the sliding brick *H*. The upper sliding brick *J* serves to close the flue system. The tops of the short flues *I*, are covered by small iron caps, readily removable for inspection of the flues.

*Becker Type Combination Coke and Gas Oven.* — The Koppers oven was highly successful and during the period 1910 to 1922 nearly 75 per cent of the by-product coking installations were of this type. However, there came to be an increasing demand for oven units of larger and larger capacity. Certain features of the Koppers oven limited the size in which it could be built. As has been explained, the products of combustion are carried from the flues on one-half of the heating wall through a top horizontal flue, to the flues on the other half. The larger the quantity of coal put through the oven, of course, the more gas must be burned, and the more products of combustion must be carried through the horizontal flue. In order to keep the resistance to flow at a minimum, the cross-section area of the horizontal flue must be increased as the amount of gases passed through it increases.

Since the horizontal flue carries products of combustion, while the vertical flues contain flames, the coal in the region of the horizontal flue requires more time for coking. This retarding of coking in the upper part of the oven is not a serious detriment with small quantities of coal, because the horizontal flue can be small, and hence affects only a small portion of the coal. However, when larger throughput is desired, and the size of the horizontal flue must be increased, this matter becomes serious.

*Distribution of Combustion Gases.* — The invention of the Becker oven made possible the construction of larger ovens, and thereby reduced the cost of coking. In this oven, the gases burn upward through all the flues in one wall simultaneously. Combustion gases are collected in "crossover" flues, from 2 to 6 in

number, which carry the gases over the coal charge.   From these crossovers the combustion gases are distributed through the flues on the other wall of the coking chamber, pass downward through these flues and out through the regenerators to the stack flue.   At the reversal, the flow of gases for the entire wall is reversed in direction.   In Fig. 63, a section of the Becker oven
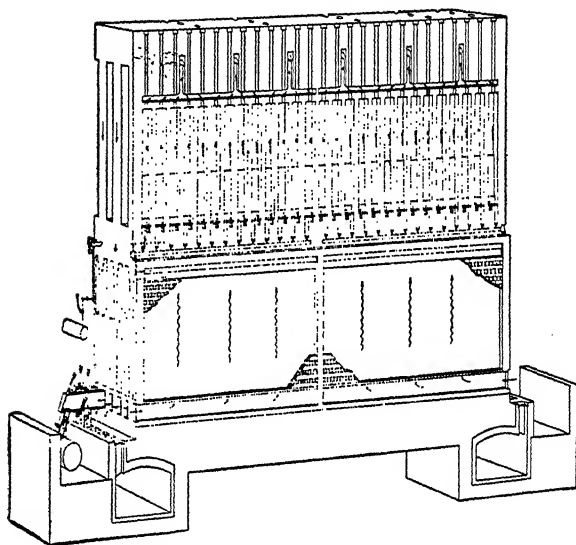


Fig. 63.   Becker Type Oven—Section through Heating Flues.

through the heating flues is shown, the arrows indicating the direction of flow of the gases.   When producer gas is used for underfiring, the gas enters through the line $\mathcal{J}$, is distributed through the regenerators from the duct $B$, and passes upward through regenerators $C$, where it is preheated.   From the regenerators, the gas is distributed to the flues $F$, where it burns with preheated air from the opposite half of the regenerator.   The combustion products collect in the horizontal flues $G$, and pass into the crossover flues $H$, which carry them over the coking chamber.   From the crossover flues, the combustion gases pass downward through flues in the opposite wall and out through the regenerators, where most of the heat of the waste gases is re-

covered, to the stack flues $A$ and $A'$.  At the reversal, the direction of flow is the reverse of that indicated by the arrows. $K$ is the main for oven gas, which is not preheated when used for underfiring.

The regenerators are divided longitudinally, to permit the separate preheating of air and producer gas.  Figures 64 and 65 show the flow of gases in a Becker oven battery before and after



PRODUCER GAS HEATING                PRODUCER GAS HEATING REVERSED
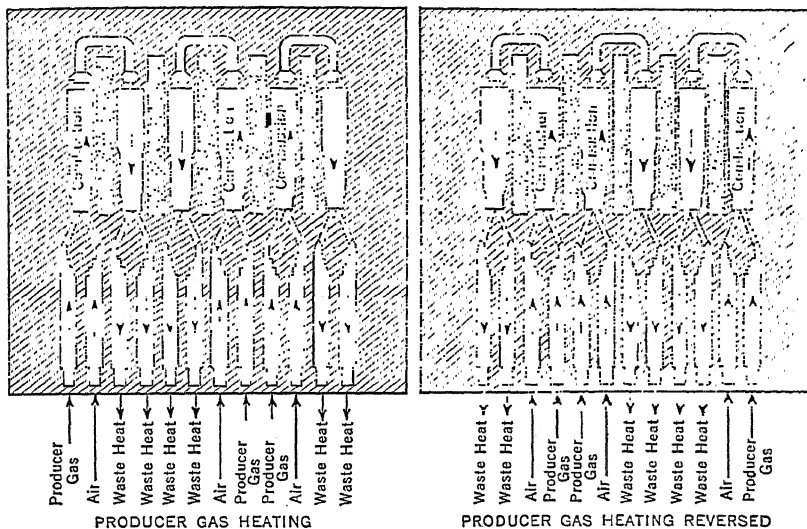
Fig. 64.  Becker Type Oven—Section through Ovens and Regenerators when Using Producer Gas.

reversal on both producer-gas and coal-gas underfiring.  A feature of the Becker oven is that it is possible to use either coke-oven gas or producer gas for underfiring, without any structural change.

Detailed descriptions of these ovens and their operation have been given by Joseph Becker [8] and Joseph Van Ackeren,[9] to which the reader is referred.

*Operation of Becker Ovens.* — Figure 66 is a section through a Becker oven plant showing regenerators, heating flues, gas piping, and oven machinery.  Coal, generally pulverized to about 85 per cent through a 1/8″ screen, is charged into the coking chamber from the larry car $G$, which travels along the top of the battery.  The charging holes $F$, are closed and the coking
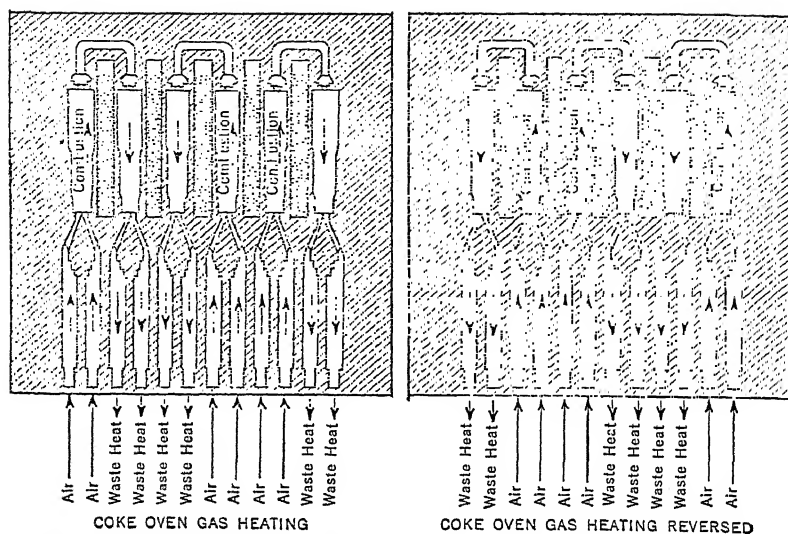
FIG. 65. Becker Type Oven—Section through Ovens and Regenerators when Using Coke Oven Gas.

process continued for a predetermined time (12–14 hours in modern ovens). The oven doors $H$–$H$, are then removed and the coke pushed from the oven by the ram of the pusher machine $J$, through the coke guide $K$, into the quenching car $M$. This car carries the coke under a water spray, where it is cooled. The coke is then discharged to a sloping "wharf," whence it is conveyed by belts to screens which separate it into the desired commercial sizes.

During the coking process, the volatile products distilled from the coal are removed through the ascension pipe $T$, into a collecting main $U$. This in turn is connected to a suction main $V$, which conveys the products to the by-product department. Liquor is sprayed into the collecting main to cool the gases and to facilitate removal of tar and ammonia.

The ovens are operated under a pressure of 3 to 5 mm. to prevent in-leakage of air and gases from the combustion flues. The suction main is under a considerably reduced pressure. The proper pressure conditions are maintained by the automatic governor $W$.

The choice of oven gas or producer gas for heating coke ovens depends upon the conditions obtaining. Where there is a ready
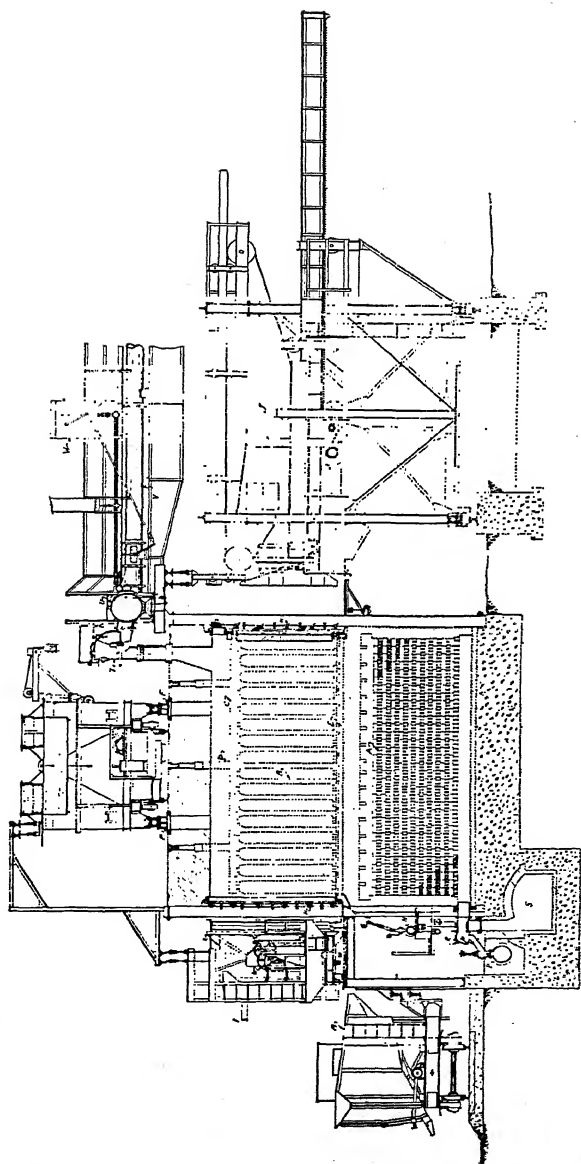
Fig. 66. Section through Becker Coke and Gas Oven—Showing Regenerators, Heating Flues, Gas Piping and Oven Machinery.

*A*—Regenerators; *B*—Verticle flues; *C*—Horizontal flues; *D*—Cross-over; *E*—Steam flue; *F*—Charging holes for coal; *G*—Larry car for coal to be charged; *H*—Doors; *J*—Pusher machine to discharge coke from oven; *K*—Coke guide; *L*—Door machine to remove and replace oven doors; *M*—Quenching car for hot coke; *N*—Fuel gas main; *P*—Producer-gas main; *R*—Air boxes; *S*—Stack flue; *T*—Ascension pipe through which distillation products pass from oven; *U*—Collecting main; *V*—Suction main; *W*—Governor.

185

market for the richer coke-oven gas, it is economical to generate producer gas of about 130 B.t.u. from the smaller sizes of coke in separate gas producers, and use this for underfiring.   The entire production of coke-oven gas is thereby released for sale.   On the other hand, there are plants in which the gas cannot be sold at a favorable price, but which have a good market for coke.   In these cases, the use of oven gas for underfiring is advantageous. As shown in the figures, producer gas is preheated before being burned, while oven gas is not.

**By-Product Recovery.** — All the products of the coking process, except the coke, pass off from the oven through the standpipe into the collecting main and thence into the suction main.   These products consist of:

(*a*) Water vapor, resulting from the moisture in the coal and from
     water of decomposition formed in the process.
(*b*) Tar, a mixture of complex hydrocarbons resulting from de-
     structive distillation of the coal.
(*c*) Light oils, consisting of benzene, toluene, xylene, etc., which
     have a low boiling temperature and high vapor pressure.
(*d*) Sulfur compounds, mainly hydrogen sulfide and carbon
     disulfide, produced from sulfur in the coal.
(*e*) Ammonia.
(*f*) Fixed gases, consisting of hydrogen, methane, illuminants
     (ethylene, carbon monoxide, carbon dioxide, oxygen,
     nitrogen), and illuminants (ethylene, propylene, etc.).
(*g*) Small amounts of naphthalene, cyanides, phenol, carbon, etc.

Of these materials, tar, light oil, ammonia, and gas are the principal commercial products.   Some commercial sulfur is being recovered in purification plants, and naphthalene, phenols, and cyanides can be recovered if conditions warrant.   The various products are successively removed from the gas in the by-product and purification departments for the dual purpose of putting the gas into salable condition and of obtaining financial return from the by-products.

The early by-product coke plants recovered ammonia by scrubbing it out of the gas with water, producing a liquor which was afterwards distilled to make either concentrated ammonia liquor or ammonium sulfate.   This is the so-called indirect process.   About twenty years ago, Heinrich Koppers introduced

the direct process, which is used extensively in modern by-product coke and gas plants. The gas, after removal of tar and condensed moisture, is passed through sulfuric acid which reacts directly with the ammonia to form ammonium sulfate. A typical flow diagram of this process is given in Fig. 67.

*Collecting Main and Suction Main.* — The distillation products from the ovens enter the collecting main from the standpipes at about 400° C. and travel from the collecting main into the suction main. Cooling and condensation begin as soon as the products leave the oven. Weak ammonia liquor is sprayed into the standpipes and collecting main. This greatly reduces the temperature of the gas and aids in the removal of tar. The suction main is the line that conveys the gas from the collecting main at the battery to the primary coolers. This main is under suction, due to the exhauster and to the action of the pressure regulator at the outlet of the collecting main.

Most of the cooling and condensation takes place in the collecting main due to the liquor sprays, although some further cooling by radiation occurs in the suction main. At the outlet of the suction main the gas temperature is 75–80° C. The heavier tar vapors and water are condensed out, and are carried along the suction main to a trap located before the primary coolers. The flushing liquor, added in the collecting main, not only cools the gas but also facilitates the movement of the condensed products, and keeps the mains free from pitch and carbon stoppages. Light tar or a mixture of tar and liquor has been used for flushing, but most installations now use ammonia liquor. Nearly two-thirds of the tar and a large amount of the water vapor are condensed before the gas enters the primary coolers.

*Primary Coolers.* — The function of the primary cooler is to cool the gas and to condense tar and water vapor. Two general types of primary coolers are in use, the direct, as shown in Fig. 67, and the indirect.

The direct type primary cooler is a cylindrical tower filled with suitable packing, over which is pumped ammonia liquor. The gas enters at the bottom and travels upward, counter-current to the flow of liquor. Tar and water condensed from the gas are carried from the cooler with the cooling liquor to suitable settling tanks. Here the tar and liquor separate by gravity, and a part of the liquor is pumped through coils over which cooling water flows. The cooled liquor is recirculated over the primary cooler as before.
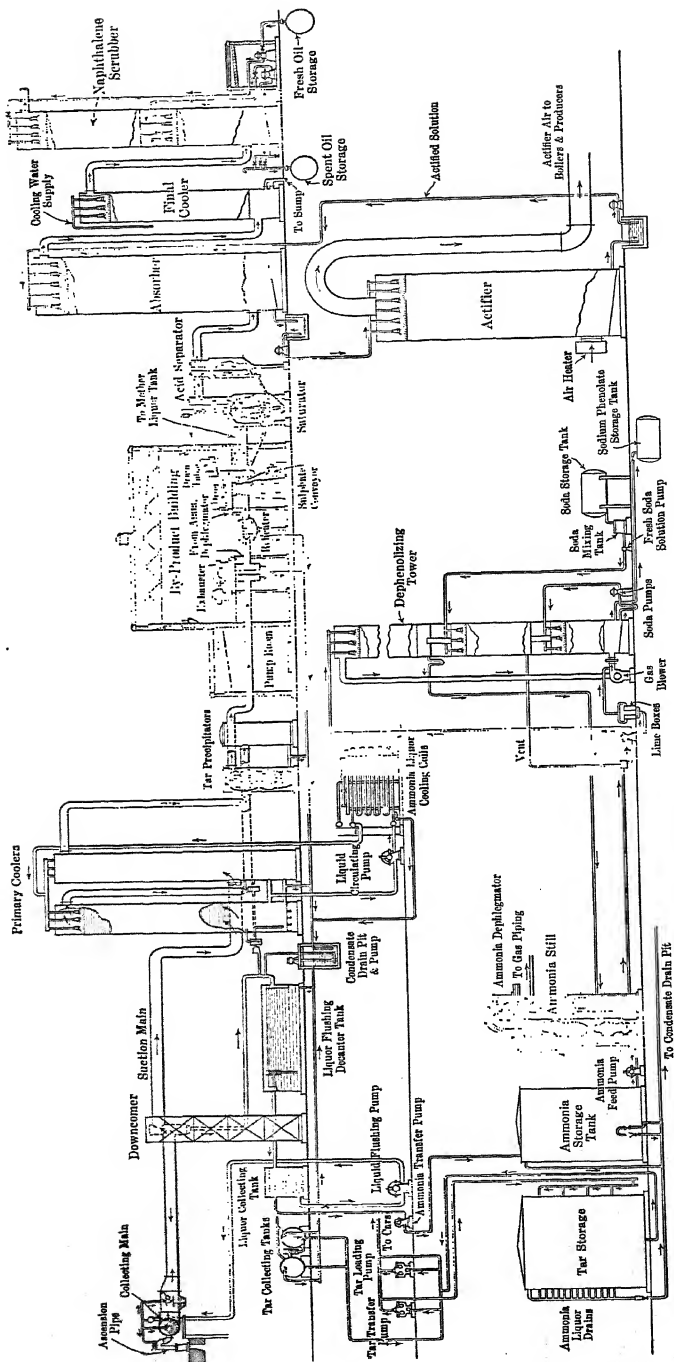
FIG. 67. Flow Diagram of Ammonia Recovery Plant.

The indirect type of cooler consists of a rectangular tank filled with tubes through which cooling water circulates. The gas, passing through the cooler, is brought into intimate contact with these tubes and surrenders its heat through their walls to the cooling water. The direction of gas flow is counter-current to that of water flow, so that the gas leaving the cooler meets the entering cooling water. Tar and water condensed in the primary cooler drain to the bottom of the cooler, whence they are pumped to separating tanks as shown.

Regardless of the type used, the primary cooler is designed to absorb the heat of condensation of the tar and water, as well as sensible heat from the uncondensed gas, and to do this without stoppages from heavy tar and naphthalene. It must provide baffling to remove mechanically entrained tar and must not offer too great a resistance to the flow of gas. It must give efficient heat transfer from the gas to the cooling medium, so that the temperature of the outlet gas closely approaches the temperature of the cooling water. The primary cooler should be equipped with an automatic temperature regulator to control the rate of water flow so as to maintain a constant temperature of the outgoing gas. In most plants, the temperature of the gas leaving the primary coolers is 20°–30° C. The gas is saturated with water vapor and carries about 5 per cent of the tar produced.[10]

*Cottrell Tar Extractors.* — In the illustration given (Fig. 67), the gas leaving the primary coolers enters the electrostatic tar precipitators. Here the gas is passed through a strong electric field, which causes the gas to become ionized and the tar particles to become electrostatically charged. The electric field is produced by maintaining a high electric potential difference between two terminals or electrodes, one of which is charged from a source of current (unidirectional or direct) and the other is grounded. The charged particles in the gas are repelled and are precipitated on the smooth surfaces of the grounded electrode.

The apparatus [11] consists of a number of vertical pipes enclosed in a steel shell, the size of the shell and the number of tubes depending on the volume of gas to be treated. The pipes are grounded through the shell. In the center of each pipe is suspended a wire which is connected to the source of high-voltage current. The gas travels upward through the pipes, and the precipitated tar drains to a seal or drain at the base of the shell.

The Cottrell equipment sets up practically no resistance to gas flow; is compact, practically self-cleaning and can be operated at a small cost.

*P. and A. Tar Extractors.* — Another type of tar extractor in extensive use is the Pelouze and Audoin (P. and A.), which consists essentially of a series of concentric inverted baskets, the walls of which are perforated with small openings. These baskets rest in a liquid seal. Gas enters at the bottom, rises through a central pipe, and then flows through the small openings in the first basket. This draws the gas into fine jets at high velocity, which impinge on the second basket, the openings of which are staggered with respect to the openings in the first basket. The tar particles coalesce and gradually flow down into the liquid seal and finally out through the overflow. The openings in the second basket are larger than those in the first, so the gas passes through them at a lower velocity and does not re-entrain the tar previously precipitated. This procedure may be repeated through two or three pairs of baskets, until the gas emerges practically tar free. Tar is pumped over the baskets to facilitate the draining of the removed tar.

The tar extractor is operated on a predetermined pressure differential, ranging from 4 to 10 inches, depending upon the conditions obtaining. This differential is maintained constant by automatically raising or lowering the level of the tar seal, thereby varying the exposed area of the baskets. An automatic regulator operates valves in the inlet flushing line and in the drain line to control the level of the seal.

*Exhausters.* — Leaving the tar precipitators the gas enters the exhauster. The function of the exhauster is to draw the gas through the suction main, primary coolers and tar extractors, and to force it through the remainder of the system to the holder. Two general types are in common use: the low-speed positive type as the Roots or Connersville, and the high-speed centrifugal type. The pressure of the gas at the exhauster outlet is generally 60 to 80 inches of water, depending upon the plant requirements. The gas temperature is somewhat increased in the exhauster due to heat of compression.

With the arrangement of equipment shown in Fig. 67, the gas leaving the exhauster is practically free from tar. It is saturated with water vapor at the lowest temperature previously encountered in the system — generally that of the primary cooler

outlet. It contains about 95 per cent of the light oils originally present, hydrogen sulfide and most of the other sulfur compounds, and a varying amount of naphthalene, depending upon the conditions of distillation and the temperatures of the scrubbing system. Furthermore, it contains 75 per cent of the ammonia formed in the distillation, the remaining 25 per cent having been scrubbed out by the flushing liquor and the condensed water.

**Ammonia Recovery.** — The next stage is the removal of ammonia from the gas. For this operation the gas is passed first through a reheater, a cylindrical steel tank containing steam coils into which exhaust steam is introduced. Here the gas temperature is raised to 50° or 60° C., to prevent condensation of water in the saturator which follows.

Immediately before the saturator, ammonia vapor distilled from the liquor (described below) is added to the gas, so that the gas entering the saturator contains all the ammonia formed in the carbonization.

The saturator is a lead-lined tank, containing a saturated solution of ammonium sulfate with some crystals of ammonium sulfate in suspension, and free sulfuric acid, about 50 grams per liter. The gas enters through a pipe communicating with the "cracker pipe" which is an inverted trough with serrated edges or slots, immersed in the saturator bath. The gas bubbling through these is brought into intimate contact with the bath, and the ammonia is absorbed according to the reaction:

$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4.$$
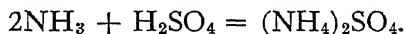
Since the bath is already saturated with ammonium sulfate, crystals are precipitated. Sulfuric acid (generally 60° BB. or 77.67 per cent $H_2SO_4$) is added constantly to the saturator to replace that consumed in the process. If the bath approaches a neutral state, the sulfate may become blue or green, owing to the formation of ferrocyanides. If the acidity becomes too high owing to excessive acid additions or to vaporization of mixture, the sulfate crystals become small and are difficult to handle. The temperature of the bath also influences the physical condition of the crystals. The presence of tar in the gas produces an undesirable brown coloration in the ammonium sulfate.

*Ammonium Sulfate.* — The production of first-grade ammonium sulfate depends upon careful control of saturator operation and

the obtaining of a tar-free gas.    A saturator temperature of 60° C. is commonly used and an acidity of the bath close to 5 per cent of sulfuric acid.

The sulfate crystals settle to the bottom of the saturator, whence they are removed by an air-lift ejector or a pump to an elevated drain-table.    The mother liquor is run back to the saturator, and the sulfate crystals are drawn from time to time into centrifugal baskets where they are washed with water, and spun until the moisture is reduced to about 2.5 per cent.    The salt is scraped from the basket, delivered to a chute, and carried to storage.    When moisture-free sulfate is required, further drying follows, a rotary kiln being used, in which the salt is brought into direct contact with hot gases.

Ammonium sulfate is white or light gray in color, contains about 0.1 per cent free acid and not less than 25 per cent $NH_3$. Some of it is employed in the manufacture of chemicals, but the greatest part is used in agriculture as a component in mixed fertilizers and as a top dressing on grass lands, crops, vegetables, orchards, etc.

*Distillation of Ammonia Liquor.* — As mentioned above, about 25 per cent of the total ammonia is recovered by distillation of the liquor, and is added to the gas directly before the saturator. The course of this liquor can be traced from Fig. 67.    As the gas is cooled in the collecting main and in the primary cooler, tar and water condense.    To this condensate is added also the liquor sprayed into the mains for flushing.    Further tar and entrained moisture are removed in the exhauster and in the tar extractor. The water absorbs ammonia from the gas until its vapor pressure of ammonia reaches an equilibrium with the vapor pressure of ammonia in the gas for the existing temperature.    Some of the ammonia also reacts with components of the gas to form chlorides and sulfides, which are almost entirely absorbed by the water. This ammonia-bearing water is termed "gas liquor" or simply "liquor."

In the example given, the tar and liquor are run to a hot drain tank where they are roughly separated by gravity, and from which the flushing is pumped to the collecting main and tar extractor.    The surplus tar and liquor are pumped to the tar separating tank, where complete separation by gravity takes place.    The tar, with a specific gravity of about 1.18, settles to the bottom, while the liquor, with a gravity of 1.0 +, rises to the

top.   From the separating tank, the tar and liquor are pumped to their respective storage tanks.

*Free Ammonia.* — Some of the ammonia in the liquor is so-called "free ammonia," i.e. salts of weak acids, such as carbonates, bicarbonates, sulfides, etc. in which the vapor pressure of ammonia approaches that of a simple water solution, and from which, therefore, the ammonia can be recovered by simple boiling.   The remainder of the ammonia is fixed ammonia, that is, salts of strong acids from which the ammonia can be recovered only by boiling with an alkali.

*Ammonia Still.* — The liquor from the storage tank is pumped to the ammonia still,[12] a cross-section of which is shown in Fig. 68. This apparatus consists essentially of a free section, a lime leg, and a fixed section.   The free section and the fixed section consist of superimposed trays, each of which contains bells or caps with serrated edges.   The hot vapors from the next lower tray pass under these bells and then bubble through the layer of liquor on the tray.   This liquor continuously overflows through a suitable connection to the tray below.   The lime leg is a vertical drum with connections for admitting the liquor from the bottom tray of the free still, and for mixing the liquor with milk-of-lime, and then causing it to pass into the top tray of the fixed section. Thus, the gas liquor first passes down through the free section counter-current to the hot vapors passing up from the lime leg and the fixed section, then passes through the lime leg, and thence through the fixed section.   Most of the steam used for expelling the ammonia passes into the bottom tray of the fixed section, although some steam is put directly into the lime leg and occasionally into the free section.   The function of the free section is to vaporize ammonia from such compounds as ammonium sulfide and ammonium carbonate which are readily broken up with steam and which require no lime treatment.   The function of the lime leg and fixed section is to expel ammonia from such compounds as ammonium chloride, which cannot be readily decomposed by steam alone.   The lime decomposes these compounds according to the reactions:

$$(NH_4)_2SO_4 + Ca(OH)_2 = CaSO_4 + 2H_2O + 2NH_3,$$

$$2NH_4Cl + Ca(OH)_2 = CaCl_2 + 2H_2O + 2NH_3.$$
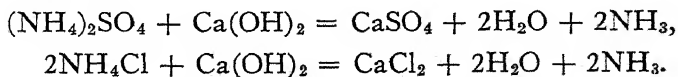
*Dephlegmator.* — The ammonia still is often equipped with a dephlegmator, which is an apparatus containing cooling elements
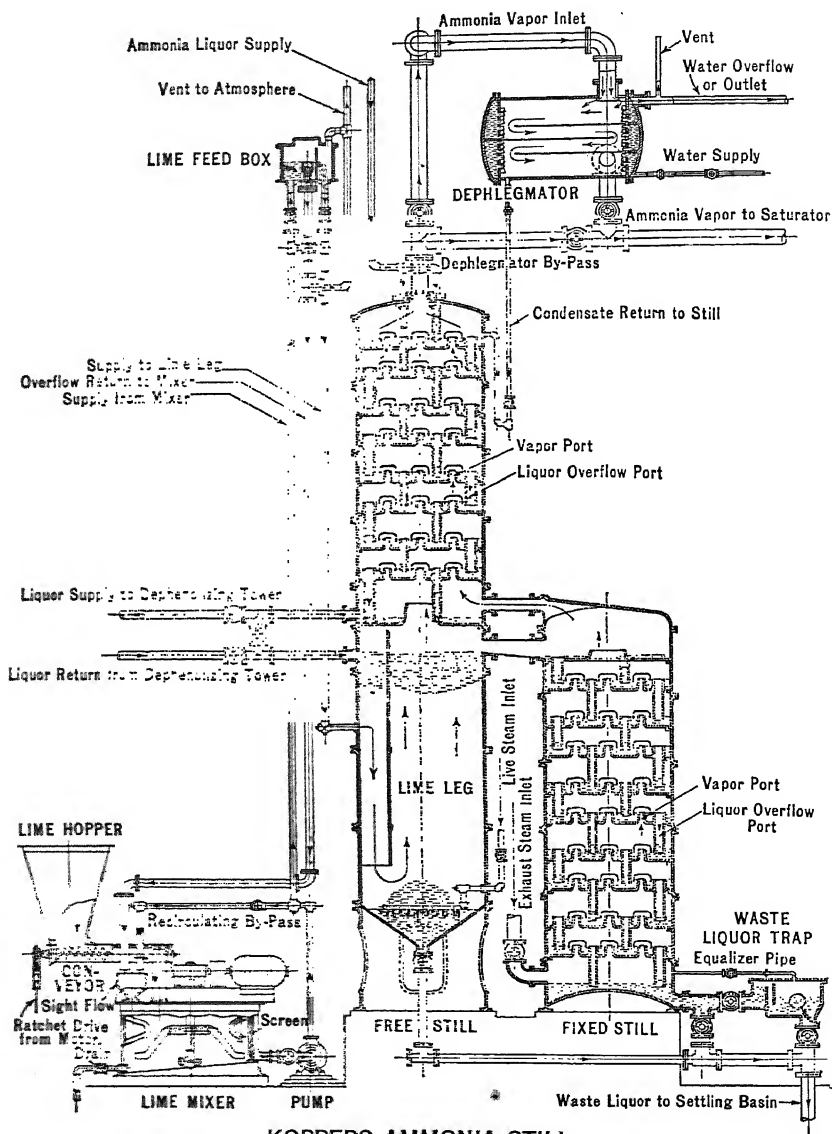
KOPPERS AMMONIA STILL

FIG. 68.

or pipes through which cold water or sometimes cold gas liquor is caused to flow. This apparatus has the function of condensing part of the moisture in the vapors from the ammonia still, which condensate flows back into the still. This has the effect of concentrating the ammonia in the vapors finally passing into the saturator or condensing apparatus.

*Still Waste.* — The liquor from which the ammonia has been expelled passes out the bottom of the fixed section of the still, together with some extra water from the steam and milk-of-lime. The volume of the so-called ammonia still waste is about 40 per cent greater than the volume of the gas liquor. Most of the phenol carried by the gas passes into the still waste. This also contains some calcium compounds — principally calcium chloride — together with some suspended excess lime and calcium carbonate. The still waste in some cases is discharged into sewers, and in many plants it is used for quenching coke.

*Phenol Extraction.* — In the illustration (Fig. 67) the ammonia liquor leaving the free still and before entering the fixed still is passed through a Koppers phenol extraction plant. In this process the liquor is treated with a large volume of recirculating vapors, which carry the phenol from the liquor. These vapors are then treated with a caustic soda solution which reacts with the phenol to form sodium phenolate. The liquor leaving the phenol plant is run to the fixed still and distilled in the usual manner. The resulting still waste is practically free from objectionable tar acids and can be discharged into streams adjacent to the plant. Sodium phenolate resulting in the process is "sprung" with stack gas, releasing the tar acids for which a ready market exists.

*Recovery of Ammonia as Liquor.* — Because of special conditions, it is sometimes desirable to recover the ammonia, not as the sulfate, but as ammonia liquor. Figure 69 is a flow sheet of a plant of this type. This plant differs from that shown in Fig. 67 in that the tar extractor is located after the exhauster. Following the tar extractor are five ammonia washers, arranged in series. These are cylindrical towers filled with wooden hurdles, over which water (gradually becoming ammonia liquor) flows countercurrent to the gas flow  The liquor from the first scrubber is pumped over the secondary cooler, and thence through separating tanks to weak liquor storage. From the storage tanks, the liquor is pumped to an ammonia still, similar to that already

shown (Fig. 68). The ammonia vapor may be run to a saturator, if ammonium sulfate is desired, but in the present example, it is cooled and absorbed in water to produce concentrated ammonia liquor containing about 20 per cent $NH_3$.
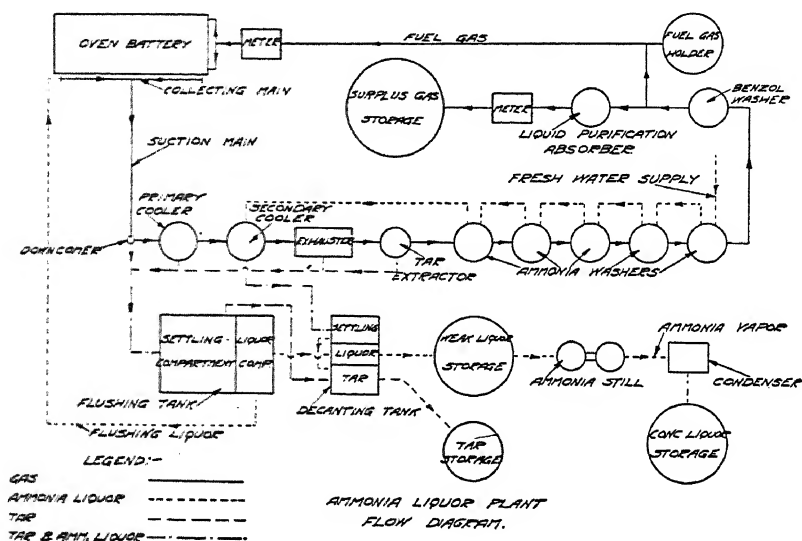


FIG. 69.

**Purification of Gas.** — In the plant illustrated in Fig. 67, the next step after the recovery of ammonia is the removal of hydrogen sulfide, or purification, as it is universally termed.

Hydrogen sulfide is formed in coal carbonization by the decomposition of pyritic and organic sulfur compounds and the reaction of the sulfur with hydrogen in the gas. Some of the hydrogen sulfide is removed in the condensing and scrubbing system, but most of it passes through. The amount of hydrogen sulfide in the gas depends on the amount of sulfur in the coal. American coals produce from 200 to 500 grains per 100 cubic feet, which must be removed before the gas is distributed. Hydrogen sulfide will cause corrosion in the distribution system and in the appliances in which the gas is burned, and the sulfur dioxide, resulting from its combustion, is a nuisance. Hence, state regulations require a very high efficiency of removal. A strip of moistened lead acetate paper suspended in the purified gas must show no

discoloration after a one-minute exposure. Under these conditions, the gas contains less than 0.1 grain of hydrogen sulfide per 100 cubic feet.[17]

The methods for removing hydrogen sulfide may be divided into two general classes — dry purification and liquid purification.

*Dry Purification.* — Dry purification as it is practiced today, consists in passing the gas through layers of iron oxide mixed with some dispersing medium as wood shavings or corncobs. The hydrogen sulfide reacts with the oxide as follows: [18]

$$Fe_2O_3 \cdot xH_2O + 3H_2S = Fe_2S_3 + (x + 3)H_2O,$$

$$Fe_2O_3 \cdot xH_2O + 3H_2S = 2FeS + S + (x + 3)H_2O.$$
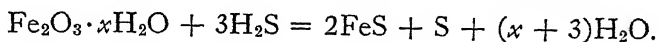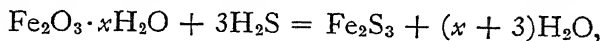
The amount of water in the hydrated oxide will vary somewhat; therefore "$xH_2O$" is used. The first reaction which is the desirable one in gas purification occurs under alkaline conditions,[17] while the second reaction occurs under neutral or slightly acid conditions.

When the oxide has become fouled or sulfided, it is revivified by air:

$$2Fe_2S_3 + 3O_2 + 2xH_2O = 2Fe_2O_3 \cdot xH_2O + 6S,$$

$$4FeS + 3O_2 + 2xH_2O = 2Fe_2O_3 \cdot xH_2O + 4S.$$
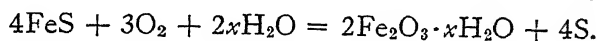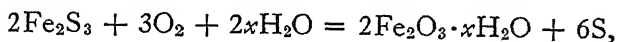
Partial revivification is carried out by reversing the flow of gas through the boxes, when the oxygen in the gas reacts with the fouled oxide. For complete revivification, the oxide is removed from the boxes, moistened with water containing a little slaked lime or soda ash, and allowed to oxidize in the air. The function of the lime or soda is to correct the tendency of the oxide to become acid during revivification, from the formation of ferrous sulfate, and also to encourage the formation of ferric sulfide instead of the ferrous, when the oxide is returned to the boxes.

In the United States, owing to a plentiful supply of cheap sulfur, no spent purification material is treated to recover the sulfur and oxide. In Europe, however, large quantities of spent oxide are used in the manufacture of sulfuric acid.

The dry purification process is generally located following the final cooler and naphthalene removal plant (described below).

*Liquid Purification.* — During recent years, there has been a rapid development of liquid purification processes. These have been of two general types, the Seaboard Process and the Sulphur Recovery Processes.
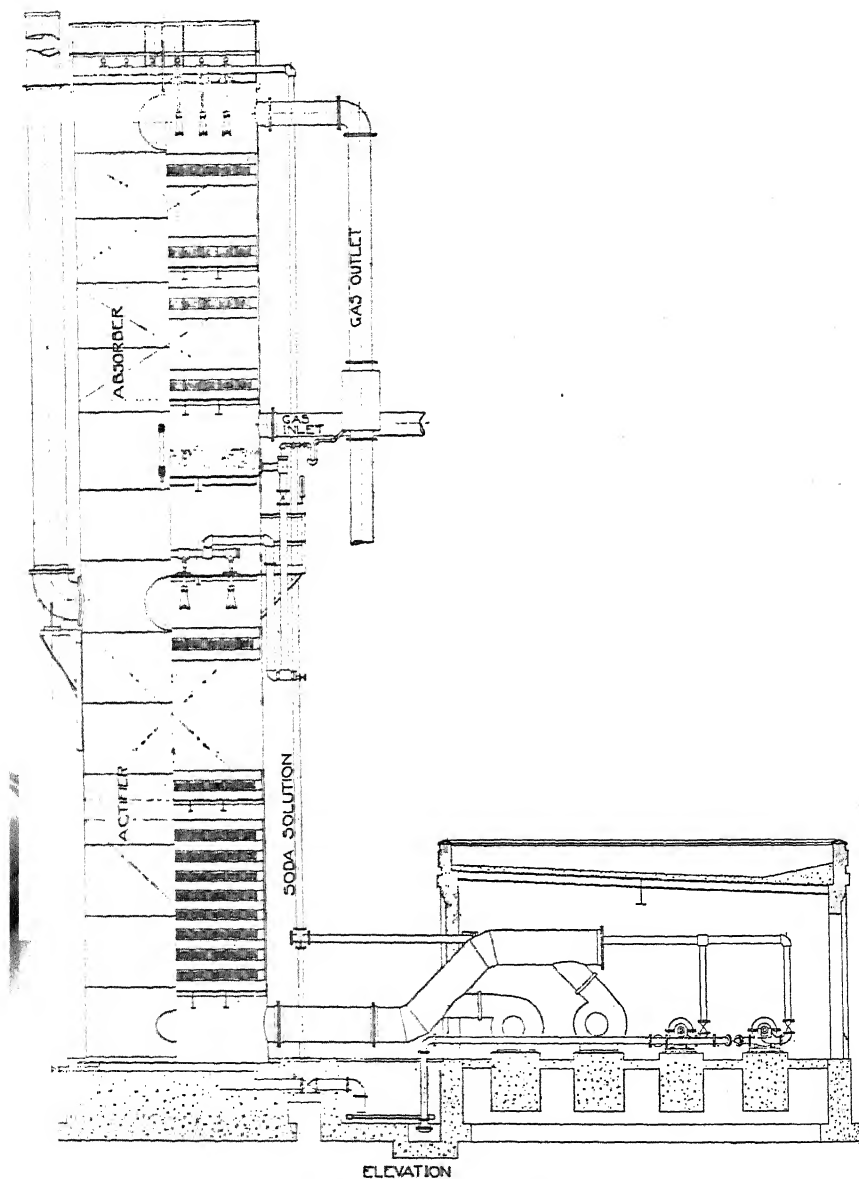
Fig. 70.   Seaboard Liquid Purification Plant.

The Seaboard Process [19] (illustrated in Fig. 67) consists in scrubbing the gas with a solution of soda ash, which reacts with the hydrogen sulfide and hydrocyanic acid in the gas (Fig. 70). The fouled solution is then aerated with a large volume of air by which the sodium carbonate is revivified and the hydrogen sulfide is carried out. This air may be discharged into the atmosphere or may be used in boilers, gas producers, water gas machines, etc. The apparatus in which this reaction is carried out is called an actifier and consists of a steel column filled with hurdles or other packing in which the fouled solution from the liquid purification absorber is treated with air to remove the absorbed impurities and regenerate the solution.

The chemical reactions involved are as follows:

$$Na_2CO_4 + H_2S = NaHS + NaHCO_3,$$

$$Na_2CO_3 + CO_2 + H_2O = 2NaHCO_3,$$

$$Na_2CO_3 + HCN = NaCN + NaHCO_3.$$
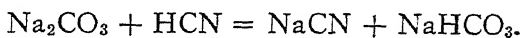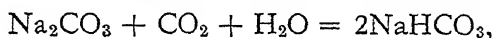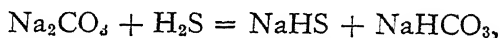
The revivification stage is the reverse of these reactions. Extensive discussions of the chemical principles of this process have been given elsewhere to which the reader is referred.[19]

*Sulphur Recovery Processes.*[20] — The sulfur recovery processes comprise treating the gas with a dilute solution of sodium carbonate (0.5 to 2%) in which is dissolved or suspended a suitable catalyst, and subsequently aerating this solution (Fig. 71). The gas is brought into contact with the solution in an absorber, where the hydrogen sulfide and hydrocyanic acid are removed from the gas. The solution is then run to a "thionizer" in which air in minute bubbles flows through the solution. This causes free sulfur to separate which accumulates on the surface of the solution in the form of a thick foam. This is run off to sumps from which the sulfur slurry is pumped to a filter. The sulfur is filtered out and the filtrate returned to the solution. The hydrocyanic acid forms sodium thiocyanate (NaCNS), and in addition some sodium thiosulfate ($Na_2S_2O_3$) is also formed. These salts accumulate in the solution, part of which is periodically withdrawn. From this liquor, the thiocyanates and thiosulfates are recovered.

The sulfur recovered has the characteristic of being very finely subdivided, and as a result has excellent possibilities for use in agriculture as a fungicide and insecticide.
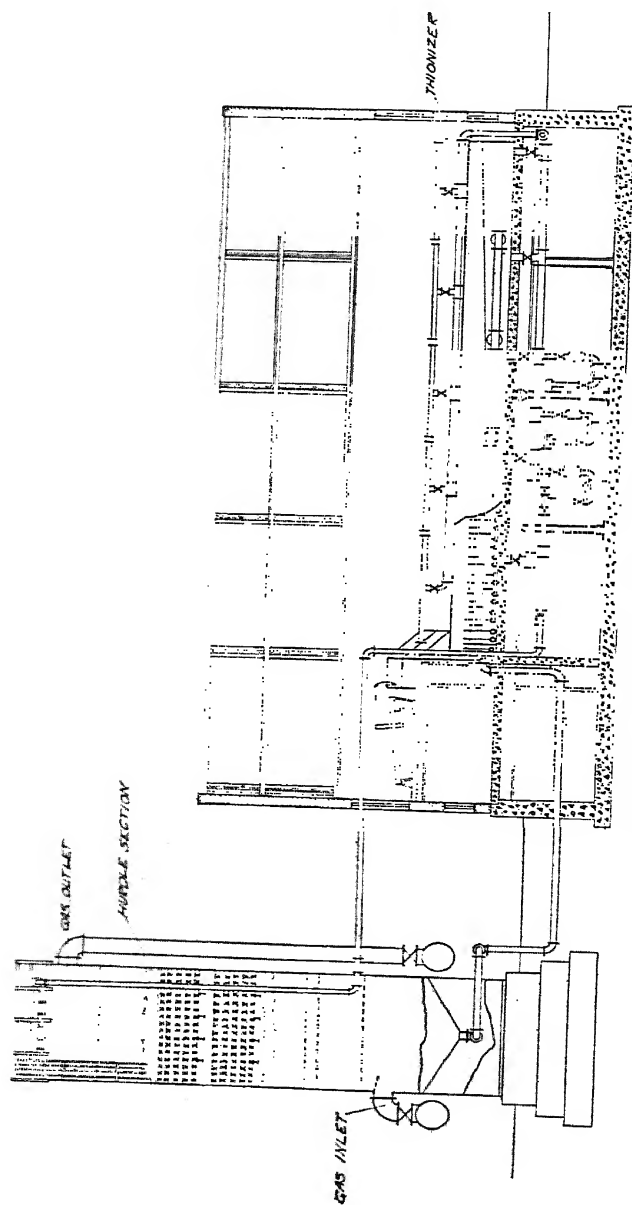
FIG. 71.  Thylox Liquid Purification Plant.

**Recovery of Light Oil.** — The gas leaving the liquid purification absorber is passed to a final cooler, a tall cylindrical tower filled with wooden hurdles, where it is cooled to about 25 to 30° C. by direct contact with water. In some plants this cooler is located ahead of the purification apparatus. The cooling also removes some naphthalene which accumulates in the final cooler water, and is skimmed off of the collecting sump at the outlet.

If recovery of light oils is desired, this is the next step. Light oils are made up of substances of the benzene series — benzene, toluene, xylene, etc., which, although liquid at normal temperatures, have sufficient vapor pressure so that the small amount present (1.0–1.3 per cent by volume of the gas) will remain in a gaseous state in the coal gas.

Of the total light oils distilled in the carbonization of coal, 5 per cent is found in the tar and 95 per cent may be recovered in scrubbing the gas. The decision as to whether light oils should or should not be scrubbed from the gas is based entirely on economic considerations. It has been calculated that light oils constitute 5.8 per cent of the original heating value of the gas.[13] When the gas is sold for city distribution, the light oils are generally more valuable when left in the gas. However, when the gas is used in a steel plant, and assigned a low value, or when the price of light oil products is high, light oils can be profitably recovered. In other words, when the light oils sold as such can show a profit over the cost of recovering, greater than their value in the gas, they are recovered.

Light oils are recovered by absorption in an oil, from which they are subsequently recovered by distillation. The oil generally used is a petroleum product termed straw oil. It has a specific gravity of about 0.88 at 15° C., will remain fluid at 4° C., should not emulsify with water, and 90 per cent should distil between 250° and 350° C.

The light oil absorbers consist of tall towers (generally in series of 2 or 3) filled with wooden hurdles. The wash oil is pumped over the towers in series, countercurrent to the direction of gas flow. In this way, fresh oil is brought in contact with the gas containing the least light oil vapors. The towers are designed so that the oil is distributed uniformly through each, and the gas and oil have prolonged and intimate contact. The gas leaving the last absorber passes on for purification.

*Stripping Still.* — The enriched wash oil, containing between 2 per cent and 3 per cent light oil, accumulates in tanks beneath

the scrubbers, whence it is pumped to the recovery plant.   Here it is delivered to the "stripping still," the object of which is to separate the light oil from the absorbent oil.   In order to conserve heat, the incoming benzolized oil is used as a cooling medium for the vapors from the still, in a vapor-to-oil heat exchanger, and then as a cooling medium for the debenzolized wash oil in an oil-to-oil heat exchanger.   Leaving the heat exchangers, the oil passes to a superheater, where its temperature is further raised by live steam, and part of the lighter fractions of the light oil distilled off.   From the superheater, the oil passes to the stripping still.   This consists of a series of superimposed sections, over which the oil flows downward while steam, blown into the lowest sections, travels upward.   The upper sections act as a separator, to remove any wash oil carried over mechanically.   Since the wash oil has a much higher boiling temperature than the light oil, very little of the former is distilled.   The vapors of steam and light oil pass through the vapor-to-oil heat exchanger previously mentioned, to a water cooled condenser.   The light oil is separated from the condensed water in a separator, and run to tanks for temporary storage.

The debenzolized wash oil is discharged from the bottom of the still and passes successively through the oil-to-oil heat exchanger mentioned above, and water-cooled coils, which reduce its temperature to 25–30° C.   It is then pumped back to the absorbers and the process repeated.   Although the wash oil acts only as an absorbent or transferring medium between the light oil in the vapor state and in the liquid state, a small loss of it occurs — not more than 5 per cent of the light oil produced — due to its being carried out mechanically by the gas from the absorbers or by the vapors from the stills.

*Treatment of Light Oil.* — The light oil as recovered in the stripping still, contains the following components, plus from 3 to 5 per cent wash oil: [17]

Crude benzol *............................about 70 per cent
Crude toluol.............................about 17 per cent
Crude light solvent naphtha...............about  7 per cent
Crude heavy solvent naphtha..............about  6 per cent

* The terms benzene, toluene, xylene, etc., are commonly used to designate pure products of definite chemical composition and fixed boiling temperature.   The terms benzol, toluol, etc., denote the commercial products, boiling slightly above and below the boiling point of the pure products.

The next step is to separate the crude light oil into its components and to prepare these for market.  The procedure followed varies depending on the products desired, i.e. motor fuel or pure products.  The flow sheet for a motor fuel plant is shown in Fig. 72.  For motor fuel production, the entire crude light oil is agitated with concentrated sulfuric acid (66° B.) for about 20 minutes.  The acid acts upon the unsaturated hydrocarbons, and other impurities, causing them to polymerize and to settle out with the acid, as acid sludge, which is withdrawn from the bottom of the agitator.  This acid sludge is sometimes discarded as a waste product, or it may be boiled with steam to recover sulfuric acid of about 40° B., and a separation of the resinous materials.  This acid is used for the recovery of ammonia from the gas.

The light oil is then washed with a 10 per cent caustic soda solution, which neutralizes any acid left in the agitator and also removes some of the phenoloid bodies.  This is followed by a water wash, to remove the last traces of caustic.

*Crude Still.* — Following the treatment in the agitator, the washed light oil is run to the crude still.  This is composed of three parts:

1. The lowest section is a horizontal cylinder, provided with both steam coils and steam sprays, for indirect and direct heating. The capacities range between 5000 and 20,000 gallons.

2. A fractionating column is mounted on the lowest section. It is composed of a series of bell sections for scrubbing the distilled vapors as they ascend.

3. A dephlegmator is attached to the upper end of the fractionating column.  This is a short horizontal cylinder containing a number of water-cooled pipes, and acts as a partial condenser.

*Distillation.* — As the temperature of the oil in the cylinder is raised by indirect steam, the lower boiling constituents are vaporized and pass up through the column.  Part of the higher boiling oils are also vaporized, but condense in the column and flow back to the drum.  The ascending vapors are washed by the descending condensate, so that only the lighter vaporized oils reach the top of the dephlegmator, where they are condensed and withdrawn.  As the temperature of the oil in the still is gradually increased, the higher boiling fractions are recovered in the same manner.  The fractionating column causes the oils to be separated in the order of their boiling points, so that the material

Fig.     Flow Diagr    Koppe        F        Oi    hed

recovered at any one temperature has a fairly uniform composition. When the temperature of the still reaches 160° C., direct steam is introduced to complete the distillation.

The distillate is separated into fractions, roughly as follows: forerunnings, motor fuel, and heavy solvent naphtha. The temperatures at which the cuts are made vary at different plants, depending upon the specifications in that particular market. The end of the distillation depends upon the upper temperature allowable for the heavy solvent. Remaining in the still are the heavy fractions, boiling above the temperature reached in the distillation. These are termed "still residue" and may be mixed with the tar, or sold separate for fuel purposes.

*Pure Products.* — When pure products are desired, the operation is different, as shown in Fig. 73. The crude light oil from the stripping still is run to what is termed the "crude still," similar in design and operation to that previously described. The cuts, based on the still temperatures, are roughly:

Forerunnings,
Crude benzol and toluol up to 130° C.,
Crude light solvent naphtha up to 160° C.,
Crude heavy solvent naphtha up to 205° C. (90 per cent).

The residue remaining in the still consists mainly of naphthalene and wash oil. This may be drained into naphthalene pans, where solid naphthalene separates on cooling. The wash oil is removed in a centrifuge and the naphthalene is washed with water. In this form, it may be sold as crude naphthalene, or in some plants, it is further purified and the pure product produced.

The fractions from the crude still are separately washed with acid, alkali and water in an agitator similar to that used for motor fuel production (see above).

*Pure Still.* — The washed products are then transferred to the pure still, which is of essentially the same design as the crude still, although larger in size. Here the products are distilled so that at least one fraction is a pure product, ready for market. The other fractions from the pure still are collected and redistilled when a sufficient amount of each has accumulated. In this manner, all of the light oil will eventually be worked up into pure products.

Motor benzol is used extensively for motor fuel. It is water white and generally has a boiling range from 80° to 135° C. It can be used alone, or may be mixed with gasoline. The presence

Fig. 73.  Flow Diagram of Koppers Benzol Recovery Plant
(Crude Fractions Washed).

of 25 per cent benzol in gasoline makes it an anti-knock motor fuel.

Benzene and toluene are used as solvents in many chemical industries, and as sources of explosives, especially toluene which is the base for T.N.T. Solvent naphtha is a solvent for rubber, varnishes, paints, etc. It is also used in cold vulcanization of rubber. All the light oil products are bases for various dyes and drugs.

*Removal of Naphthalene from Gas.* — As has been previously pointed out, it is often desirable to leave the light oils in the gas, especially when the gas is intended for city distribution. Naphthalene, however, must be eliminated. Naphthalene is formed from the cracking of hydrocarbons on the hot oven surfaces. It has the peculiar property of condensing from the gas in the solid phase, and if not removed, will cause stoppages in distribution and service lines, valves, and meters. The amount of naphthalene present in the gas depends upon the amount formed in the coking process, upon the naphthalene vapor pressure of the tar and condensate with which the gas has previously been in contact, and upon the temperature of the gas.

Naphthalene removal is accomplished by scrubbing the gas with an oil. A naphthalene-free coal-tar distillate or a water-gas tar oil may be used, but in most cases a petroleum distillate is employed, generally ordinary gas oil. The desideratum is the scrubbing of the gas with a very small amount of oil so as not to remove light oils, and at the same time to obtain intimate contact between the gas and the scrubbing medium. Various types of scrubbers are used to achieve this end, such as simple packed towers, centrifugal scrubbers, rotary washers, etc. One type — the Koppers process [15] (Fig. 74) — employs a packed tower having two sections. In the upper section, small increments of oil are charged periodically at high speed and under high pressure, while in the lower section, a large volume of oil is constantly recirculated at a relatively high rate.

The gas enters at the base of the lower section and passes upward through the lower and upper sections, countercurrent to the oil flow. The reduction in heating value of the gas is practically zero.[16]

The spent oil from the naphthalene scrubber may be used for carburetting water gas, for fuel oil, or for any purpose for which the original oil was suitable. If so desired, the naphthalene can
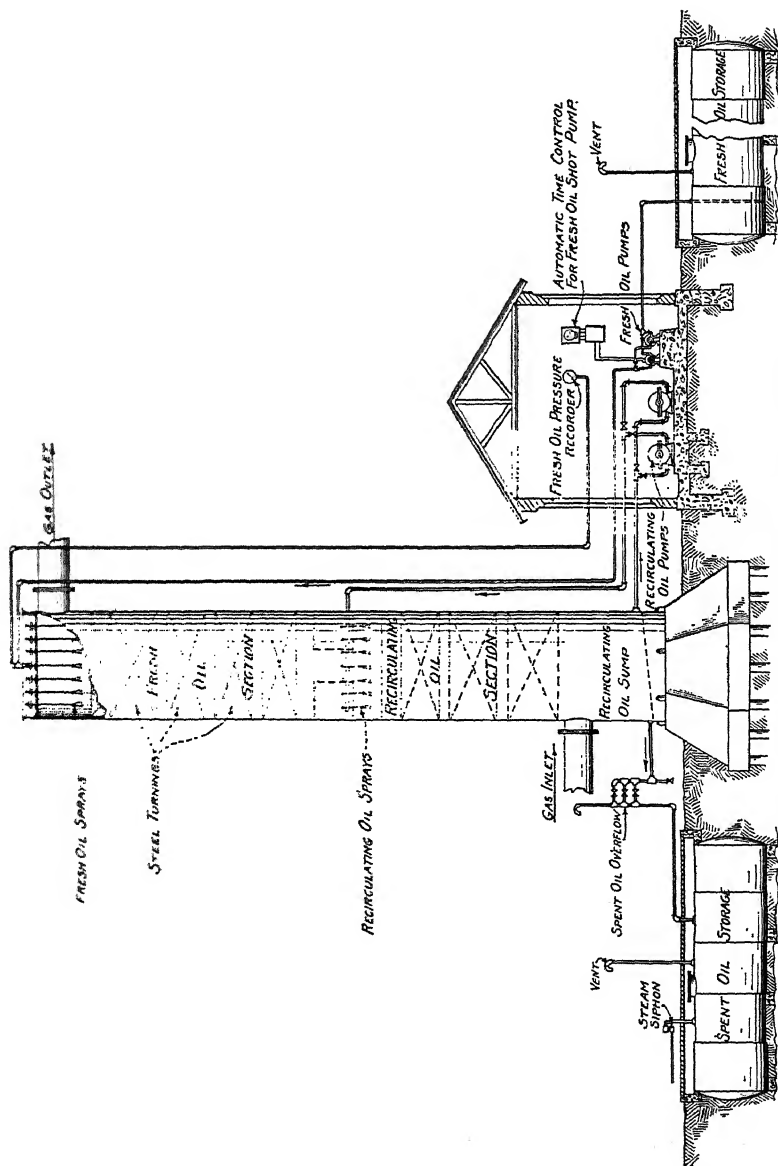
FIG. 74. Koppers Type Naphthalene Removal Plant.

be recovered and purified. At the present time, however, practically all of the naphthalene recovered is produced in light-oil plants or by tar distillers.

The gas leaving the naphthalene removal plant contains carbon disulfide and other organic sulfur compounds as impurities, as well as some oxygen and moisture, which are not generally removed. The gas is run to the holder, ready for distribution to consumers.

**Tar.** — One important by-product of coal carbonization remains to be discussed, namely, the tar. The gradual condensation of tar from the gas in the collecting main, suction main, primary cooler, exhauster, and tar extractor has been explained, together with the separation of the liquor and the tar (page 187). Practically no by-product coke plants refine their own tar. It is shipped in tank cars or run by pipe lines to a tar distillation plant where it is worked up into finished marketable products.

*Tar Distillation.* — The tar as it is received at the tar plant contains small amounts of moisture. This may be removed in a dehydrating still, in which the tar is run in thin layers over hot surfaces. Heating thick layers of tar containing moisture will cause foaming and spattering, due to entrapped steam bubbles. The dehydration is carried to 170° C., when all the water is removed, together with any ammonia present, most of the light oils, and some naphthalene. The light oils are treated in the same manner as the light oils scrubbed from the gas, previously described.

*Refined Tar.* — The dehydrated tar, termed "refined tar," is sometimes used without further treatment in roofing and paving materials, or in paints and insulating compounds. In most cases, however, it is distilled in a tar still. The condensate evolved is collected in appropriate fractions, depending on the use for which they are intended. Figure 75 is a flow sheet of a typical tar distillation plant.[21]

The first fraction (170°–235° C.) contains tar acids and naphthalene. The distillate is cooled in crystallizing pans, the naphthalene separated in a centrifuge, and the oil treated with caustic for the recovery of the tar acids, phenols and cresols.

The second fraction (235°–270° C.) is also cooled for naphthalene recovery. The oil may be mixed with the residue of Frac-

tion No. 1 from which tar acids have been removed, and sold as creosote oil.  The composition of creosote, its gravity, and the amount of tar acids and naphthalene contained may be varied according to specifications and market conditions.
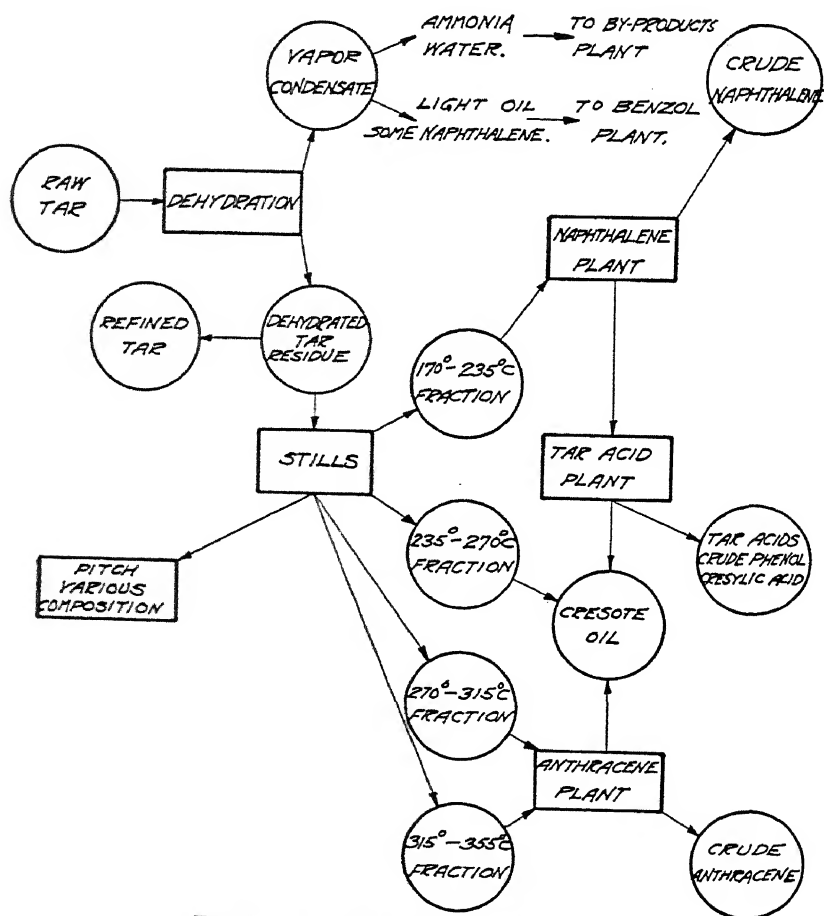


Fig. 75.    Tar Refining Plant Flow Sheet.

The fractions above 270° C. are varied according to the products desired.    Anthracene is recovered in the fractions from 270° to 315° C., and from 315° to 355° C.    However, not much anthracene is being produced in the United States at present, owing

to market conditions. The higher boiling fractions are generally added directly to the creosote oil. The quality of pitch remaining in the still depends upon the temperature to which the distillation is carried. If the distillation is stopped at 270° C., a soft pitch is obtained, which is used in roofing and waterproofing. As the distillation is continued, a harder pitch results until eventually pitch coke remains.

The tar still is of the horizontal boiler type, and is fired by coal or gas. A common condenser is provided, and the receiver is changed for each fraction. The process as described is an intermittent one, although several continuous processes are used with success.[22, 23] As previously noted, the manner of fractionating the tar depends upon the products desired, and will vary from time to time and from place to place.

Many of the by-products of the coking industry are raw materials for other processes, which produce dyes and perfumes, medicinals and antiseptics, explosives and varnishes. The tar distilling plants manufacture road materials, roofing materials, wood preservatives, disinfectants, paints, and pitches. The pitches, depending upon their hardness, are used for waterproofing, roofing, briquetting, storage batteries, carbon electrodes, targets, cores for foundry work, fuel and pitch coke.

**Yields of By-Products.** — The amount of by-products obtained per ton of coal varies somewhat depending upon the type of coking apparatus used, conditions of carbonization, and the kind of coal. Of these factors, the first cannot be changed without rebuilding the plant. As to the second factor, every plant operates to obtain the maximum yield of profitable products, and, generally speaking, conditions that have an adverse effect on one by-product have a similar effect on other by-products. Hot oven tops and prolonged exposure of distillation products to high temperatures, for example, decrease the yield of ammonia, decompose the light oils, and crack the gases into products of lower heating value. Consequently in all well-operated plants this condition is avoided, insofar as is possible.

*Kinds of Coal Used.* — The greatest variation in by-product yields is due to different kinds of coal used. With 100 per cent high-volatile coal (30–36 per cent volatile) a higher yield of tar and gas is obtained, but the coke yield is decreased and the coke is generally friable. To improve the quality of the coke, as well as

to increase the yield, some semi-bituminous coal is mixed with high-volatile coal. The amount may be as high as 50 per cent, but in most plants it is between 15 per cent and 30 per cent. The admixture of a semi-bituminous coal decreases the yield of gas and tar, but with properly selected coals, the coke pieces are larger and the coke is harder and stronger. The selection of coals is governed by the cost and availability of the coals and the markets for coke and by-products.

*Yield of Products.* — The following are the average yields of products obtained for the United States as a whole in 1930, including all types of plants and all coal mixes employed:

| | *Yields per Net Ton Coal* |
|---|---|
| Coke................................................ | 1380 lb. |
| Tar................................................. | 9.2 gal. |
| Ammonium sulfate or equivalent.................... | 23.5 lb. |
| Light oil........................................... | 3.1 gal.* |
| Gas—total.......................................... | 11.1 M cu. ft.† |

\* Average for plants recovering.
† Of this amount 4.3 M cu. ft. were used in the coking process.

In a modern, efficient coke and gas plant, of the type previously described, the yields of products (other than coke) are about 10 per cent higher than the figures given. Also producer gas can be used in the coking process, releasing the entire production of coal gas for distribution.

**Economics of By-Product Recovery.** — The fundamental object of any industry is to make a profit, either directly or indirectly, and by-product recovery is warranted only when it works toward that end. The economic soundness of by-product coking depends upon obtaining a higher unit differential between the value of the diversified products and the cost of raw materials and operation than the differential that can be obtained in beehive coking.

The following example is based upon Bureau of Mines data.[25]

VALUE OF BY-PRODUCTS AND OF COKE PER TON OF COKE PRODUCED
1930

| | *By-Product* | *Beehive* |
|---|---|---|
| Ammonia and its compounds....................... | $0.50 | 0 |
| Light oil and derivatives......................... | 0.53 | 0 |
| Surplus gas—sold and used....................... | 1.75 | 0 |
| Tar—sold and used.............................. | 0.69 | 0 |

| | By-Product | Beehive |
|---|---|---|
| Value of coke produced.............................. | 4.42 | $3.43 |
| Value of breeze and miscellaneous..................... | 0.27 | 0.02 |
| Total value of products...:....................... | $8.16 | $3.45 |
| Value of coal used per ton of coke................... | 5.04 | 2.54 |
| Value of products minus value of coal used............ | $3.12 | $0.91 |

From these figures, by-product coking as compared with beehive coking is economically feasible when the cost of the process does not exceed the cost of beehive coking by more than $2.63 per ton of coke produced.

The higher value assigned to coal for by-product plants is due in part to the fact that the by-product plants are generally located near to the point of consumption of the major products, whereas beehive ovens are generally located near to the mines; consequently the value of the coal for by-product plants includes a variable amount for freight charges. While the figures shown above apply to the country as a whole, individual installation will vary widely both in coal costs and amount derived from the products.

However, with the development of by-product coking, it was found possible to make good coke out of coals that could not be satisfactorily treated in the beehive oven. Therefore, a complete study of any modern by-product coking proposition must take into account not only the above consideration, but a comparison of the cost of the various coals deliverable to the by-product plant *vs.* the cost of the coals deliverable to the competing beehive ovens.

*Cost of By-Products.* — Two general methods are used for determining the cost of by-products.[26] According to the first method, no direct labor or overhead is charged against the by-product, but only such items as handling and sales expense. These are deducted from the selling price of the by-product and the balance credited against the raw material cost of the primary product. Thus the by-product itself can show no profit, its sole function being to reduce the cost of the primary product. This procedure is desirable only when the by-product is distinctly subordinate to the primary product, for example, pitch coke in a tar refinery.

Under the second method, the entire manufacturing costs are distributed among the several products, the distribution being

based on chemical analyses of the products, relative weights, current market values, or an empirical standard ratio. As the selling price of each product is known, the separate profits can be determined. This method is used where several products have appreciable value, as in a by-product gas plant.

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<div align="center">PROBLEMS</div>

The following problems are typical of some of those that are encountered in the planning of a by-product coke plant.   Fundamental to the solution of such problems is a knowledge of the coking behavior and by-product yields of the coal that is to be used.

The *coking behavior* of a coal is determined by previous experience with such coal at existing plants, or in the absence of such experience, by practical oven tests. Such experience or such tests give the following essential information:

1. The proportions of available coals required in a mixture to produce the best coke.
2. Optimum pulverization of coal mixture chosen.
3. Weight per cubic foot of coal mixture at optimum pulverization.
4. Width of oven, temperature and coking time required to produce the best coke.
5. Total yield of coke and yields of various commercial sizes of coke and breeze.
6. Heat required for coking.   This is technically known as the "underfiring requirement" and when the ovens are heated with coke oven gas is expressed as B.t.u.'s required to coke one pound of coal.   When the ovens are heated with a producer gas, the underfiring requirement is usually expressed as a percentage which means the weight of coke used in the producers stated as a percentage of the coal charged into the ovens.   Thus 14 per cent underfiring means that 280 pounds of coke are consumed in the producers for every ton of coal charged in the ovens.   It, therefore, follows that by subtracting the percentage underfiring from the total percentage coke yield, we have the percentage net coke yield after the producer requirements are satisfied.

The *by-product yields* of a coal mixture for which practical data are not available are best determined by tests made in laboratories which have special equipment for this purpose, and which have an abundance of practical and laboratory data for comparative purposes.   Following are the most important by-product data required:

1. Cubic feet total gas produced per ton of coal and heating value of this gas in B.t.u's per cubic foot.   It should be stated whether these figures are calculated before or after recovery of light oil.
2. Gallons of tar produced per ton of coal.
3. Pounds of ammonia ($NH_3$) produced per ton of coal.
4. Gallons of light oil produced per ton of coal.

In solving problems 25, 26 and 27, suppose it is desired to build a by-product coke plant to supply 8,000,000 cubic feet of gas per day to a certain city.   This gas is to have an average heating value of 530 B.t.u's per cubic foot.   A coal mixture is to be used consisting of 80 per cent high volatile Kentucky coal with 20 per cent Pocahontas coal.   The following data have been obtained from coking tests and from practical experience with closely similar mixtures:

Optimum pulverization 85% through 1/8 inch.
Weight of pulverized coal per cubic foot, 49.5 lbs.
Optimum oven width, 18 inches at discharge end tapering to 16 inches at pusher end
Optimum coking time, 17 hours
Yield of coke over 1/2 inch, 69% of coal charged.
Yield of breeze under 1/2 inch, 5% of coal charged.
Underfiring requirement, 1,200 B.t.u's per pound of coal.

The yields of by-products are as follows:

Gas (530 B.t.u's per cubic foot).................11,400 cubic feet per ton coal

(Calculated afrer recovery of light oil)

Tar...........................................11.4 gallons per ton coal
Ammonia (NH₃)................................. 6.5 lbs. per ton coal
Light Oil..................................... 3.8 gallons per ton coal

25. Calculate the number of ovens required to produce the 8,000,000 cubic feet of gas per day as *surplus gas*. The ovens are to be 40 feet long and the height from floor to top of coal charge is to be 10 feet. In this case part of the gas produced is to be used for heating the ovens and this, of course, is calculated from the underfiring requirement. What would be the production of coke over 1/2 inch?

26. Assuming a plant of coke ovens built under the conditions of Problem 25, what would be the production of surplus gas and of coke over 1/2 inch per day, if the coking time were lengthened to 20 hours?

27. After building the plant under the conditions of Problem 25, it is desired to install gas producers for the purpose of heating the ovens so as to release the entire production of coke oven gas for city consumption. The underfiring requirement will be 13.5 per cent and 50 per cent of the breeze products can be used in the producers. How many tons of coke over 1/2 inch will have to be consumed in the producers per day, and what will be the daily production of coke and salable gas?

28. Under the conditions of Problem 25, how many cubic feet of gas must be burned per day in the oven flues from the pusher side to the center of the battery as compared with the gas burned from the center of the battery to the discharge side? Note that the ovens are tapered and that the underfiring per pound of coal must be approximately the same throughout the battery.

29. For producing pig iron from a certain ore mixture, 1,800 pounds of coke over 3/4 inch are required per ton of pig iron produced. Assuming the use of the same coal mixture as in Problems 25–27, and assuming that the coke between 3/4 inch and 1/2 inch (nut coke) is 2 per cent of the coal charged, calculate the daily production of surplus gas, tar, ammonia and light oil from a plant operating in connection with a blast furnace making 900 tons of iron per day.

30. In a plant operating under the conditions of Problem 29, how many pounds of sulphuric acid (60° Bé) will be required per day for the conversion of all of the ammonia into ammonium sulphate? What will be the daily production of ammonium sulphate?

31. A by-product coke plant is to be designed to coke 1,000 tons of coal per day —the coal mixture being the same as in the preceding problems. Twenty-five per cent of the total ammonia is to be removed in the ordinary condensing apparatus, and the remainder is to be scrubbed out with water in the form of a weak liquor containing 1 per cent NH₃. How many gallons of water will be required per day for this scrubbing operation?

32. In the plant designed as in Problem 31, the gas enters indirect primary coolers at 80° C., and its temperature at the outlet of these coolers should be 20° C. The cooling water enters at 15° C. and leaves at 65° C. The inlet gas is saturated with water vapor: Neglecting the heat content of the ammonia and the suspended tarry matter and all radiation losses, calculate the number of gallons of cooling water per hour that must be supplied to the primary coolers. How many gallons of ammonia liquor will be collected from the coolers per day?

33. A by-product coke plant is designed to produce 10,000,000 cubic feet of total gas per 24 hours. With the old style P. and A. tar extractors there is an average difference between the inlet and outlet gas pressure of 8 inches of water. Assuming a power cost of 1.85¢ per kw. hr., calculate the annual saving in cost of gas compression that is to be gained by substituting electrical precipitators which have a negligible pressure differential.

34. A by-product coke plant is to be designed to coke 1,000 tons of coal per day, the coal mixture being the same as described for Problem 25. Twenty-five per cent of the total ammonia is removed in the condensing apparatus in the form of a gas liquor, analysis of which shows 4.5 grams per liter free ammonia and 6.3 grams per liter fixed ammonia. The lime purchased for operation of the ammonia still contains 92 per cent CaO. Calculate the number of pounds of lime theoretically required per day.

35. Chemists have long been desirous of developing a process by which the hydrogen sulphide in coke oven gas could be used directly or indirectly to furnish the $H_2SO_4$ required for recovering the ammonia in the form of ammonium sulphate. Taking the coal mixture used in Problem 25, and assuming that the gas contains 350 grains of hydrogen sulphide per 100 cubic feet, calculate how much excess of or deficiency of sulphuric acid this would theoretically furnish as compared with the requirement for the production of ammonium sulphate from this coal.

36. In the sulphur recovery processes practically all of the hydrocyanic acid in the gas is converted into sodium thiocyanate. Assuming that the gas from the plant in Problem 31 contains 30 grains of HCN per 100 cubic feet, calculate the number of pounds of NaCNS that will be formed per day and the amount of sodium carbonate that will be required for this formation.

37. A by-product coke plant is to be designed to coke 1,000 tons of coal per day, the coal mixture being the same as in Problem 25, and light oil is to be recovered. Practical experience shows that the wash oil leaving the benzol scrubbers should contain 3 per cent by volume of light oil, while the oil returning from the wash oil still to the scrubbers will contain about 0.3 per cent light oil. Calculate the number of gallons of wash oil that must be pumped over the scrubbers per hour.

38. A coal mixture produces 3.5 gallons of light oil per ton of coal in a by-product coke plant and 15 per cent of this light oil is pure toluene. Calculate how many pounds of T.N.T. can be theoretically made from the annual production of a plant coking 1,000 tons of coal per day.

39. In a by-product coke plant operating in connection with a blast furnace and steel plant the tar competes directly with fuel oil for the operation of open hearth furnaces. The tar has a heating value of 157,000 B.t.u's per gallon. The fuel oil has a heating value of 135,000 B.t.u's per gallon and costs 5¢ per gallon. How much must the steel company receive for its tar to make it worth while to sell the tar for distillation purposes and purchase fuel oil?

# CHAPTER VII

## FILTRATION

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Filtration is the art of removing suspended solids from liquids or gases by means of a porous medium, which medium allows the liquid or gases to pass through, but retains the solids. A filter is an apparatus for obtaining such a separation. The solids form what is known as the filter bed or filter cake and the liquid passing through is called the filtrate. Only the filtration or separation of solids and liquids will be discussed in this chapter. The discussion will also be confined to standard types of filter presses which are in general use in the chemical industry. This apparatus consists of a chamber practically enclosed with a filter cloth. The mixture of liquid and solids is forced into this chamber, the solids remaining on the filter cloth as a filter cake, the liquid passing through the filter cloth. In some forms of filter presses suction is used instead of positive pressure.

**Rate of Flow.** — In the separation of solids from liquids by means of filter presses, several factors govern the rate of flow of the filtrate per unit of filter area. These factors are mainly the following — (a) the character of the precipitate or solids being filtered, (b) the viscosity of the liquid, (c) the filtration pressure, (d) the temperature of the liquid being filtered, and (e) the filter medium.

As different solids deposit and retard the progress of filtration differently, no definite or even fairly accurate filtration formulae can be devised for all cases.

**Interspaces.** — Crystalline or rigid solids occupy very definite spaces and during filtration they pack at random adjacent to each other so that definite interspaces result. These interspaces are not all straight, but are connected with each other by means of tortuous pore systems. In filtering such solids, the rate of filtration and cake deposit is very rapid. If the grains are irregular, the smaller ones will become lodged in the interspaces

left between the larger grains, thus reducing the size of the capillary pore system and naturally reducing the rate of filtration. Although the filtration proceeds rapidly through the tortuous interspace pore system, it will be seen that the cake thickness does not indicate the length of the capillary pores. The same crystalline grains of one cake remixed with liquid and refiltered will deposit in different adjacent positions under the same filtration conditions and slightly shorten the general length of the capillary pore system in one place where it may be lengthened in another.

It can easily be shown that the grains or crystals of filter press cakes are not arranged to give the closest contact. When an apparently dry cake is hammered or jolted in any receptacle the cake soon becomes covered with a mass of the liquid. This shows that the solid particles were wedged together in random positions and were held apart by films of liquid about all the grains. During the jolting, the lighter liquid in the films and pores rises to the top and the solid particles rearrange themselves in a much closer contact, thereby forcing the lighter liquid to the top.

**Pore Space.** — The question of pore space is of prime importance in all filtration. It is of special importance in determining the rate of filtrate flow. This question will be more readily understood if we assume, for instance, that the solid particles forming the cake are all small spheres, as of sand, for instance, of uniform size. Several uniform symmetrical arrangements are possible with such spheres. They can be loosely piled so that one sphere only touches four others, or they can be piled in various arrangements to the point where one sphere touches twelve others. This last arrangement is the closest possible. It has been shown that the percentage of volume of pore space in the loosest arrangement is 47.64 while the same volume percentage is only 25.95 for the closest arrangement of particles. These percentages are independent of the diameter of the spheres as long as the spheres are all of uniform size.

Mixtures encountered in filtration engineering never offer these ideal conditions of uniform size of solid.

All sizes and shapes of solid particles must be dealt with.

**Small Particles.** — The natural assumption is that in practice the smaller particles will lodge in between the larger irregular

particles and materially reduce the lowest volume percentage noted in the foregoing ideal case of spherical grains. The very reverse is generally the case. They may reduce the size of the individual pores, but they also materially increase the number of pores and the total volume of pore space. In the case of a filter press cake like that commonly handled in carbonated sugar juices, having 50 per cent moisture, and where the specific gravity of the solids is about 2.9, we find the following to be true: In 100 grams of this cake, the fifty grams of water present will occupy 50 cc. of space. The 50 grams of solids will occupy 17.25 cc. of space. The total volume occupied by the 100 grams of cake is therefore 67.25 cc. The percentage of volume occupied by the solids is only 25.65 while the percentage of volume occupied by the moisture is 74.35, which is considerably in excess of the pore space of the loosest arrangement of uniform spherical particles, namely; 47.64 per cent.

The explanation for this extremely high percentage of pore space is, in all probability, that the solid particles are enveloped in films of moisture, and furthermore the particles are wedged into very loose random positions leaving innumerable fine circuitous pores that give a total of a very large pore space percentage. This is certainly true when the effect of hammering or jolting such cakes is noted as already described.

Irregular solids can naturally be packed into very small spaces where there remains very little void space between them, or they can be heaped in a much looser arrangement. Cementing them together into the form of hollow shells will give still greater pore space percentage. Add to this the space occupied by the films of liquid surrounding the particles and one can see how the entire percentages can be changed in an infinite number of ways.

Increased permeability does not depend on increase in the number of pore spaces, but on increase in the size of the individual pores or pore spaces. Water will run through a bed of spherical pebbles 10 mm. in diameter, where, for instance, there are one hundred relatively large pores, much more quickly than it will through a bed just as large composed of fine sand spheres 0.1 mm. in diameter, where we may have tens of thousands of minute interspaces.

**Capillary Tubes.** — The reason for this is that a filter press cake is a mass containing innumerable fine circuitous capillary

tubes through which the filtrate must flow. The larger the tubes the more easy the flow. This follows from the laws of capillarity.

Poiseuille's formula for the flow of liquids through capillary tubes is

$$Q = \frac{KHD^4}{L},$$

where $Q$ is the rate of flow of the liquid, $H$ the pressure head, and $D$ and $L$ the diameter and length of the capillary tube, while $K$ is a constant, depending on the viscosity of the liquid among other things.

The pressure head, $H$, is equal to the difference between the pressures on the two sides of the press cake and may therefore be expressed as $p^1 - p^{11}$. The filtration rate increases directly with the pressure head. As the filtration rate varies with the fourth power of $D$ it will increase very rapidly with increase in the pore spaces.

This is also the reason that a large number of very fine capillary pores will show a decreased rate of percolation when compared with the rate through fewer larger pores.

Filtration rate will also increase rapidly with decrease in viscosity of the liquid. As viscosity decreases with increase in temperature, filtration will be more rapid with a hot than with a cold liquid.

If the length and mean diameter of the pore system in filter press cakes could be determined, the above formula would give the approximate flow of filtrate through a filter press cake. It is evident that the cake thickness cannot be accurately taken as the length of the capillary pores on account of their irregular shape, although the length of these pores bears a definite relation to the cake thickness. It is also evident that the diameters of the different pores will vary considerably at different points.

It has been found, experimentally, that the foregoing formula holds good for the percolation of water through beds of sand, clay and powdered chalk. It has been confirmed even with the percolation of water and solutions through filter paper. In these instances $D$ represents the distance between solid particles in the cake, $L$ the cake thickness and $H$ the difference in pressure. The filtration rate is found to vary inversely as the cake thickness and directly as the fourth power of the distance between particles.

The formula will be only approximately confirmed in filtration in chemical and most metallurgical industries. The chief reason for this discrepancy will be found in the fact that the distance between particles and also the length of the capillary channels changes during filtration. The length of the tortuous pore passages can scarcely be formulated mathematically and is much greater than the cake thickness. This alone may account for much of the discrepancy between formula and fact.

*Rigidity of Particles.* — Permanent rigidity of the individual particles has a decided bearing on the matter. Certain particles may be relatively rigid under a light filtration pressure while they may flatten out under higher pressure, with a consequent lessening of pore space. For example, thin filter press cakes in leaf type filters, one quarter of an inch thick, are soft and mushy on account of the high moisture content between the solid particles. If filter press cakes of the same material are increased to one inch in thickness, the outer surface is soft, but the layer next to the filter fabric, which in thin cakes was soft, has become relatively firm and compact. The moisture is lower and consequently the particles in these inner layers must have rearranged themselves under the superimposed impact of new particles. This arrangement has not only changed the distance $D$ between the particles but it has also changed the length of the circuitous pore system.

This is particularly true in carbonated sugar juice filtration where the lime cake contains not only particles permanently rigid but also a high percentage of flocculent precipitate of lime carbonate and organic lime compounds. These floccules are not by any means all permanent, nor is their shape permanent in most instances. This change in shape alone will entirely change the capillary system of pores, as such a cake grows in thickness and the pressure is naturally increased to force the filtrate through the growing capillary pores.

**Rate of Flow.** — What is true here may be true of most filter press cakes that contain a mixture of rigid and semi rigid solids.

According to Professor W. K. Lewis the law governing the rate of filtration flow may be solved by the following equation:

$$\text{Rate of flow} = \frac{KPM}{VN},$$

wherein $K$ is a constant varying with the nature of the liquid and its viscosity, $P$ equals the pressure and $V$ the volume of flow of filtrate, while $M$ and $N$ are constants which vary with the nature of the precipitate, etc. The constants for each solution have to be determined by special tests.

This formula is really another expression of the Poiseuille formula already mentioned, with the exception that the Poiseuille formula mathematically expresses the value $V$ in terms of flow through capillary tubes, or pore spaces.

*Gelatinous Particles.* — The instant gelatinous precipitates, or colloids enter into the problem, conditions change. Purely gelatinous particles flatten out and entirely block the pores of any filter. The less rigid the particles are the finer the resulting pores and the lower the rate of percolation will be. This brings in the question of plasticity of solid particles.

Clayey materials are solids evidently composed of rigid particles enveloped by films of gelatinous colloidal materials. This being the case it will be seen why the rate of flow rapidly decreases in filtering such materials. The gelatinous coatings are non-rigid and therefore diminish the percolation as filtration proceeds.

There are other elements entering into the theories of plasticity of filter press cakes, such as extreme fineness of particles, interlocking particles shapes, capillarity or liquid film actions between particles and varying viscosity of the liquids in question.

In filtering sugar juices, for example, all of these play an important part. Here inorganic and organic precipitates, rigid particles, colloids, and permanent and non rigid floccules must be dealt with.

*Temperature.* — The problems here as in other chemical industries are both chemical and physical, and in carrying out the operation the chemists and engineers should co-operate. The engineer knows that increased temperature of previous treatments may increase the rate of filtration. The chemist must see that this temperature properly coagulates colloids and yet produces a perfectly smooth, firm, porous filter cake and, furthermore, that the purifying reactions sought are complete under these conditions.

It is a fact that the carbonated sugar juices filter most readily when the temperature is high and the resulting cakes are washed more easily, whether extremely hot water or comparatively cooler water is used.

**Washing Filter Press Cakes.** — In washing cakes formed in pressure filters of the leaf type, the wash water pressure should be lower than the filtration pressure. The wash water consumption will be lower if it is not forced through the cake at a high velocity. The water should not be too hot, either, as it then tends to shorten the life of the filter cloth.

In cakes that have resulted from filtering chemical solutions containing salts or compounds that are liable to crystallize or solidify at certain lower temperatures it is absolutely necessary to keep the wash water hot in order to prevent this crystallization.

*Wash Water.* — When filtration is discontinued, the pores of the filter cake are filled with the liquor being filtered off. The first action of the wash water or other liquid is to displace this residual liquor. Therefore the liquor coming from the filter cocks will at first have the same density as during filtration. When the wash water has displaced all of this liquor ahead of it and has reached the filter cloth, dilution starts, as shown by the density or other test. In order to ascertain the best temperature for washing, curves graphically represent these results very well. Any change in the drop after displacement is finished, may either indicate a solvent action or a decreased pump pressure. Decreased pressure during washing shows decreased displacement. If pump pressure is constant a break in the drop of the curve indicates solvent action of some kind.

Where the density of the displaced liquor during washing can be measured by means of a hydrometer, that is the simplest way. Curves should be plotted and different temperatures and pressures tried until the least dilution is shown. A very sudden and continued drop indicates that a perfect displacement of liquor has taken place.

*Pressure.* — As previously mentioned, it is advisable to wash at lower pressure than the original filtration pressure. A higher pressure means a greater volume of outflow during washing and a possibility of hurrying the wash water through the "weak spots" of any filter press cake. A dilution and gradual break result. Furthermore the operator may close a valve a minute or so too late in any case after completed washing and two minutes excessive washing means a much larger volume of dilution at a higher pressure than it does at a lower.

*Dilution.* — Where the displaced liquor or solution is not dense enough to show on a hydrometer, as is the case with cyanide

solutions in the treatment of gold and silver ores, the displaced solutions must be titrated from time to time. Here the saving in wash water is not as important, however, as it is with hot chemical solutions that must be subsequently evaporated, and where the operator wishes to obtain absolutely pure liquor, free from any dissolved cake impurities.

In any of the curves obtained, the exact percentage of dilution can be calculated. Simply calculate the entire area enclosed by the wash curve and ordinate and abscissa; then calculate the area enclosed by the drop line and the vertical from the highest point from the top.

This dilution area compared with the entire area shows the percentage of dilution. If the amount of cake be known and the moisture content, then it is a comparatively easy matter to calculate the per cent of actual water used per ton of cake.

**Filtration Aids.** — The filter medium and the filter cake must be kept porous. Theoretically, the meshes of the medium should be fine enough to retain the solids and free enough to permit the filtrate to pass unhindered. This would always be true if the particles of solids being filtered were of uniform size and shape. Practically this condition is never met with in filtration engineering. In nearly every case the solid particles vary in size, shape and even in structure.

*Filter Medium.* — As a result, the meshes of the filter medium must be either fine enough to hold back the smallest solid particles, so that the filtrate is clear from the outset, or the pressure at the beginning of filtration must be sufficient to give the filtrate a high velocity so that the meshes of the medium will rapidly become throttled or clogged by solids packing in over the filter medium. These packed solids then become the real filter medium for the subsequent filtration. In this latter case, however, the filtrate runs cloudy until the meshes have been clogged by solids.

In some cases the meshes cannot be made too fine, because they soon become covered with a slimy impenetrable layer of semisolids that greatly impedes further filtration. Again, using a more open mesh and causing the first solids to form the real filter layer, thus necessitating a cloudy filtrate at the beginning of operation means refiltering of this cloudy portion. As a result, this difficulty is often overcome by precoating the loose

filter medium with a socalled aid to filtration. The function of this aid is to prevent throttling or clogging and also to eliminate the cloudy first filtration, thereby allowing free filtration. In this case the excessive pressure necessary for forcing the filtrate through the extremely fine pores of a closely woven fabric is obviated because the precoating becomes the medium and allows the filtrate free passage.

*Pore System.* — This will be more readily understood if we assume, for instance, that the particles used for precoating are all silica spheres of uniform size, lodged in closest contact. The total void spaces remaining between the spheres will then be well over 45 per cent of the total cake volume, which is plenty large enough for filtrate passage. As this ideal condition of uniform particles is never met with, it will be seen that in practice these small openings soon retain even smaller particles, which in turn will leave a continuous capillary pore system for the passing of filtrate, yet fine enough to retain all solids or semi-solids. This pore system will retain all the fine particles that a closely woven fabric will, and offers less frictional resistance to the passage of filtrate. The strands of vegetable filtering fabrics generally swell upon becoming wet and this increases the frictional resistance to the passage of filtrate. If the pressure is raised to offset this defect minute non-rigid solids are liable to be forced through the medium.

A precoating of granular or crystalline materials results in a very fine network pore system that does not become contracted through the expansion of the solid precoating particles upon contact with the filtrate.

Very often granular and crystalline materials are used for the purpose of precoating, and in order that the pore system shall not be too fine and compact the precoating is formed under a reduced filtration pressure at the beginning. The same is true of the following filtration, for as the solids deposited through filtration form new layers for the following filtration, these new layers must not be made too compact and impermeable by a high filtration pressure.

By gradually increasing the filtration pressure, the first layers are, even when precoatings are not used, loosely deposited, thus allowing the following liquids to pass with ease. Then, as the filtration pressure is increased near the termination of cake building, the rate of outflow will not fall as rapidly and the cake

particles will be forced more tightly together after the necessity of actual porosity has ceased to exist.

**Precoating.** — Precoatings are especially valuable where gelatinous or albuminous substances are being filtered. Without precoating the first filtrate runs cloudy and the gelatinous particles soon form a thin and almost impervious coating over the filter medium. It is often practically impossible to scrape or spray this coating from the cloth. Where coating mediums are not used the clogged cloths are sent to special washing machines.

Consequently, it is of advantage to try out different forms of precoating in filters where the cloths are washed directly in the filter and select a precoating which adheres rather loosely to the cloth and can easily be separated from it by a spray flushing arrangement. This is true even when the aid to filtration is mixed directly with the material to be filtered, as a more or less porous deposit results in any case where crystalline or porous solids are mixed with non-rigid, colloidal particles.

The most common aids to filtration are: kieselguhr, long fine crystals of sulfate of lime, saw-dust, bone char, lignite, sand asbestos pulp, paper pulp, etc.

*Kieselguhr*, known also as infusorial earth, fossil meal, filter cel, diatomite, diatomaceous earth, is found in most parts of the world, Europe, Africa, Australia and North and South America. As it is made up of the skeletons of minute water plants, varying in shape and size, according to the species, the samples of kieselguhr from different parts of the earth vary in microscopical structure. Good kieselguhr is almost pure silica and should be relatively free from chalk or calcium carbonate and clay. Spanish and Algerian kieselguhr contain over 2 per cent calcium carbonate and must be cleaned with acid before it becomes inert to most chemicals. Good kieselguhr should show a preponderance of long needles under the microscope. These needles or diatoms, with their cells or interspaces full of air, when deposited on the filter cloth, interlace over each other thus forming a very light and permeable felt-like medium which not only intercepts all suspended impurities but has a wonderful brightening and purifying effect on most liquids.

American sugar refineries have installed modern Kelly, Sweetland and Vallez filters as a result of the advantages of filter aids and the Taylor bag filters are being rapidly scrapped.

Dimness of sugar juices means minute particles in suspension and impurities in the whole process. Little attention is now paid to color as long as the juices are bright, sparkling and crystalline clear. Diatomaceous earth and paper pulp are of the greatest aid in securing such bright filtrates. Realizing this, types of Sweetland, Kelly and Vallez presses have been developed and patented for this purpose in order to combine the advantages of using precoating or filtration aids and saving labor, cloth, liquid and heat.

The quantity of filter aid to be used depends on the quantity of gums, colloids, or pectinous bodies present. Owing to its porous nature, kieselguhr is very light, weighing in cases as low as 8 lbs. per cu. ft. Consequently it is easy to suspend it in water or other liquids.

Even though filter aids are mixed with the liquids being filtered, at times it will be of advantage to pump a small quantity of the filter aid mixed with water or filtered liquids into the filter first, thus giving the cloths a precoating. This is particularly of advantage where the colloids being filtered are apt to throttle the cloth pores before these pores are sufficiently covered with the particles of filter aid.

Kieselguhr and paper pulp are of great benefit in filtering chemical solutions containing freely suspended colloids.

*Bone char* as an aid to filtration can be used like kieselguhr. It decolorizes oils, sugar juices, and other chemical solutions and patents exist covering its use in leaf and older filters. It is more costly than diatomaceous earth and paper pulp, and in order to be used economically provision must be made for its regeneration when its absorbent action is spent.

In 1785 Lowitz discovered the decolorizing effect of charcoal on liquids This discovery was first used for decolorizing brandy. In 1793 Kehls discovered that the decolorizing effect of animal char was much more powerful than that of charcoal. Figuier and Magnes continued Kehls' experiments in 1812 and found that the decolorizing effect of animal char was just as great on colored plant juices. This led Charles Derosen to introduce the use of animal char into the sugar industry in 1812. In 1822 Anselme Payen recommended the use of animal char for purification of drinking water.

Lignite was at one time used like bone char. It decolorizes, but not as effectively as bone char.

*Saw-dust.*—In 1883 Paul Casamajar patented the use of saw-dust as an aid to filtration. After treatment with caustic soda and thoroughly washing, its action is said to be like that of diatomaceous earth. Provision was also made for regenerating this saw-dust when its absorbing power was spent. On account of the cost of preparing saw-dust and regenerating it, this process has been abandoned.

At times other aids to filtration may serve a double purpose, such as the use of lime in order to neutralize acids and also form insoluble compounds that become precipitated with other impurities in the cake.

All good aids in filtration should be crystalline or rigid in structure in order to produce a felted effect, with a continuity of pores, already described.

Nuchar, Carbrox, Norit, Darco, Kelpchar, etc. are trade names for some of the carbons on the market today.

**Filter Mediums.** — Under this head may be considered paper pulp, sand, vegetable fiber, precipitates, porous stone, saw-dust, wood, straw and fabrics of cotton, wool, hemp, hair, metal, asbestos, etc. Paper pulp is used to a larger extent in filtering sugar juices, sand in water filters; while porous stone, wood and fabrics of wool, metal and asbestos are used in filtering certain corrosive materials.

*Fabrics.* — The chemist will have most to do with the fabrics such as cotton, wool, hemp, metal, etc. Cotton cloth is probably the most important of the fabrics.

The material, weave and strength of filter fabrics depends on the industrial purpose. Fabrics have the advantage of being easy to handle in case of washing and renewing. They are used chiefly to retain the solid particles held in suspension and are of value only where a definite cake mass results through filtration. Where the solids filtered are crystalline, or rigid, or a mixture of rigid solids and colloids, the use of filtration aids are unnecessary. Where a definite cake mass becomes the real filter medium fabrics alone may be used. If a fine colloidal scum results that soon impairs filtration of a large amount of liquid, filter fabrics are of little economic value, unless used in conjunction with a filter aid. This is especially the case where this scum cannot be sprayed or flushed from the fabric. Other aids such as bone char, diatomaceous earth, sand, sawdust, paper pulp, etc.,

should then be resorted to in conjunction with fabrics if necessary. Definite cake masses very often result when filtering alkaline or acid solutions that destroy ordinary vegetable and animal filter fabrics.

· *Metallic Fabrics.* — As a consequence of this, there are on the market valuable metallic fabrics that withstand the action of these chemicals. These fabrics are not screen gauze of fine delicate texture, but are woven out of multiple metal strands like cloth. They are easy to clean and very durable. They are also of high value where filtration aids are used.

There are also combinations of wire and asbestos, wire and cotton, wire and ramie, etc. These are valuable in the chemical industries where corrosive liquors are to be filtered.

### FILTERS

**Classification of Filters.** — According to the principles utilized for the separation of solids and liquids, filters may be classified or divided into groups as follows:

*False-bottom tanks, classifiers, and dewaterers.* — This class of filters depends upon gravity to separate the solids from the liquid. False bottom tanks retain the solids, permitting the liquid to flow through a filter medium in the bottom of the tank. In classifiers and dewaterers the solids settle out while the liquid or sludge flows at a limited rate, thus permitting continuous operation. This equipment has been developed for mining and other large scale operations where the particles are relatively heavy and settle out easily.

The term *expellers* is used to designate a type of machine in which mechanical pressure is employed to eliminate water from solid material such as wood pulp, coarse feed, ground oil-bearing seeds, beans, etc.

*Water filters* are designed to separate a very small amount of solid from a large volume of liquid. Beds of sand are frequently used for this purpose, employing gravity flow. In smaller mechanical equipment charcoal as well as sand is used, the flow being obtained by means of positive pressure. Water purification is often accompanied by chemical treatment for clarification or purification. For this purpose aluminium or iron sulfate followed by chlorine is often used.

*Centrifugal machines* depend upon centrifugal force for separation of solid and liquid. By this method the separation of the

liquid is very rapid and complete. This method is used for a very wide variety of materials ranging from crystalline salts, paper pulp, clothing being cleaned, to the separation of cream from milk.

*Hydraulic presses* utilize very high pressures, resulting in high extraction of the liquid and the production of a hard very compact cake. They are used very largely for the separation of oils and fats from vegetable materials, preparation of sugar juices, wine, cider, etc.

*Air and gas filters* are constructed to separate solid or liquid particles from gases and will be discussed in chapter XIII.

**Filter Presses.** — The term filter press is used to designate the most widely used type of filter employed in the chemical industry. They may be divided into two classes depending upon whether the flow of liquid is induced by positive pressure or by vacuum. The pressure filters are practically all intermittent in operation, while the vacuum filters are generally of the continuous type. A filter press is designed to utilize a large area of filtration surface in order to give a large filtration capacity. Another very important consideration is the amount of labor required for operation of the filter press.

**Plate and Frame Filters.** — These filters are used on a greater variety of material than any other class of filters. They consist of a number of loose plates or plates and frames clamped together to form a series of hollow chambers. These plates or plates and frames are placed vertically upon a frame made up of two end supports, rigidly held together by two horizontal steel bars.

The hollow chambers are formed either by the recessed plate, or the flush plate and hollow frame, clamped together. The faces of the plates are grooved, pyramided or ribbed, except at the edges, where they are machined to form a joint surface. The whole plate is covered with a filter cloth, forming a filter surface where the plates are grooved, pyramided or ribbed and acting as a gasket on the machined surface. A closing device, operating on one end of the press against a movable head, pushes the plates or plates and frames along the horizontal bars making a tight joint. The plates or plates and frames are pushed along by hand when putting on or removing the filter cloths or when discharging or closing the press.

The two types of plate presses are illustrated in Figs. 76 and 77. Figure 76 shows the non-washing recessed type with center feed and open delivery.    Figure 77 shows a corner feed, four eyed, washing, closed delivery plate and frame filter.
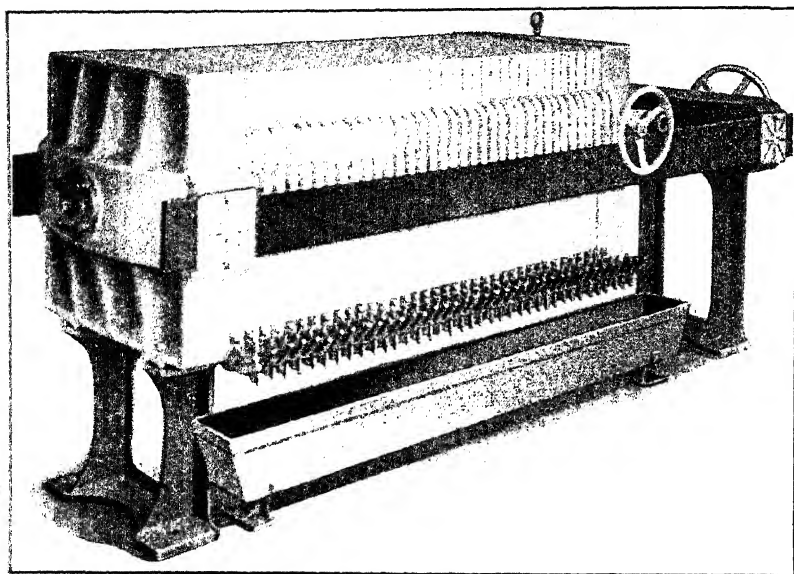


FIG. 76. (Plate and Frame)Filter Press, Non-Washing, Center Feed.
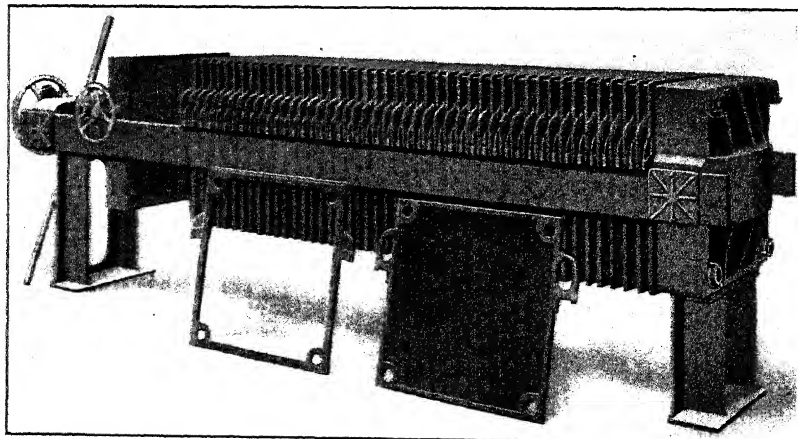


FIG. 77.   Plate and Frame Filter Press, Corner Feed Washing Type.

In operating the plate or plate and frame filters the cloths are placed over the plates, the press closed and locked. The material to be filtered is then pumped into the press. The solid matter remains in the chambers formed by the recessed plates or the plates and frames, the filtrate passing through the cloths and out of the press. When filtration is finished, generally determined by the pressure shown on the pressure gauge and the rate of flow of the filtrate, the pump is stopped, the press unlocked, the plates or plates and frames separated by hand, the cake dumped off into a conveyor of some kind, if the cake is of value and is to be saved. If the cake is of no value it can be flushed away with water after dumping. In case the cake needs washing in the plate and frame press, the wash water or some solvent is pumped through the press before opening. After cleaning off the cloths and the contact surfaces of the plates or plates and frames the press is ready for another cycle.

Practically all manufacturers make round and square presses and in certain cases triangular, center or side feed, one-, two-, three-, or four-eyed recessed, and plate and frame wood or iron, and hand or hydraulically closed.

**The Sweetland Pressure Filter.** — The filter body or shell of the Sweetland press is a cylindrical casting divided along its horizontal axis into two halves. These two halves are hinged together in the back, the two halves being machined along their contact edges with a groove in the upper half containing a composition gasket forming a watertight joint when bolted together by the swing bolts as shown in Fig. 78. This figure shows the filter open, so that the leaves may be seen, also the lower half with its counter-weight, the inlet, discharge, and sluice pipe connections.

*Operation.* — The operation of the Sweetland Filter is as follows: Close and lock the filter, get the material to be filtered into the filter, build the cake to the desired thickness (cakes must not come together), flush out the excess sludge by compressed air, get the wash water into filter, exhausting the compressed air gradually so as not to disturb the cake, wash the cake, expel the excess wash water, blow air through the cake if it is desired to dry it, release the air pressure and open the filter. If desired to get the cake out dry, give a few puffs of air on the inside of the filter leaves to loosen and drop the cake. If the cake can be

flushed from the filter, use sprays instead of air.    After cleaning, if necessary, the filter is ready for another cycle.

The labor required to operate the Sweetland Filter press is considerably less than that required for a plate and frame press, particularly if the cake can be flushed out.    As the filter cloths are sewed on the leaves replacement of cloths is more difficult.
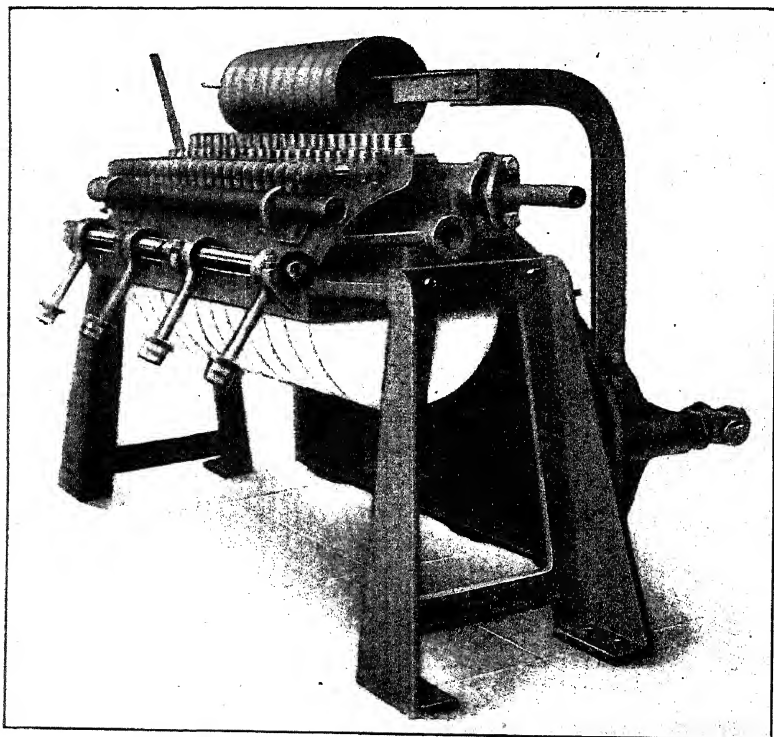


Fig. 78.   Sweetland Pressure Filter, Filter Open

The *Auto Filter* shown in Fig. 79 consists of a wrought steel cylinder with part round filtering elements.   The cylinder is divided above the horizontal center into two parts, hinged together at the back.   When closed, a watertight joint is formed and the parts are held together by the bolts and lugs shown. The inlet and outlet pipes and steam connections enter the bottom of the shell, and the air and overflow are located on top.

The filter leaves are made of heavy wire fabric and are hung vertically on a carrier which is attached to a revolving manifold at each end, so that the leaves rotate during filtration. The filtrate from each leaf passes through a separate pipe to the shaft manifold, half of the leaves discharging at each end of the filter. Outside of the revolving manifold shaft are arranged
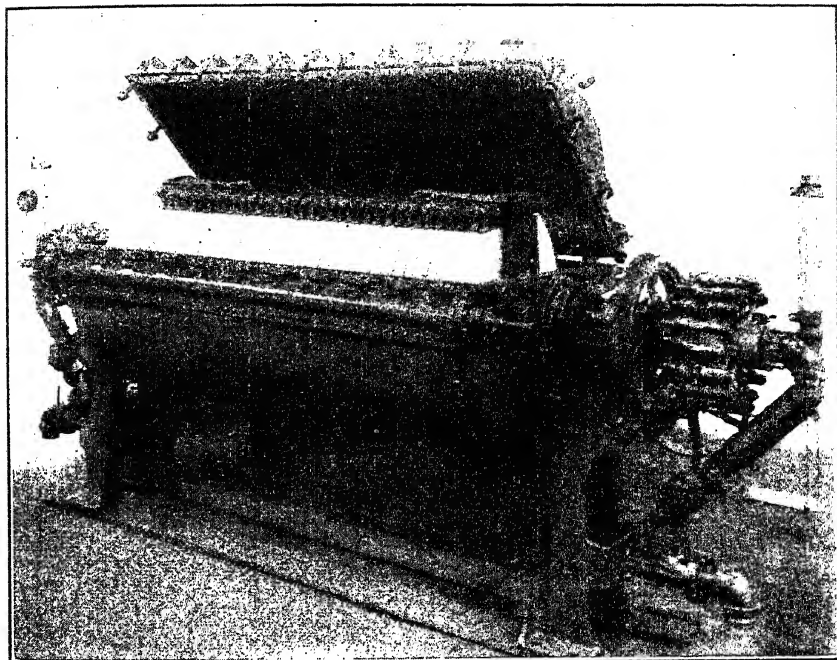


FIG. 79. Auto Filter, 900 Sq. Ft. Filtering Area, Interior View.

glass tubes, one for each leaf, so that the action of each leaf may be observed. A cock is provided for each leaf so that if any one runs cloudy, the cock on that particular leaf may be turned off. Each leaf is covered with filter cloth and held in position by two bronze cap nuts so that any defective leaf can be easily replaced. The filter is equipped with a sluicing device and can be equipped for dry or wet cake discharge.

This filter has met with great success in sugar factories where white cane sugar is made direct from the sugar cane by treating the sugar juices with activated carbon. It is adaptable to many operations in chemical plants.

**The Kelly Pressure Filter.** — The Kelly Filter consists of a supporting frame, steel pressed shell, filter carriage, filter leaves and quick locking head mechanism. The cast iron head is mounted on wheels which run on the outer track on top of the supporting frame, while the rear end of the carriage runs on tracks inside the shell. The leaves are all of the same length but of different widths, and are made of rolled steel pipe and double crimped wire screen. The forward corners of the leaves are connected to openings through the head, through which openings the filtrate passes out of the press. The filter cloth is made in the form of bags and sewed on the leaves.

A cycle of operation consists in closing and locking the filter, building the cake, expelling the excess sludge, washing with water or other solution, expelling the excess wash water, drying the cake by letting air blow through cake, and then opening the filter and discharging the cake.

Figure 80 gives a good view of a Kelly Filter open, showing the leaves, etc.
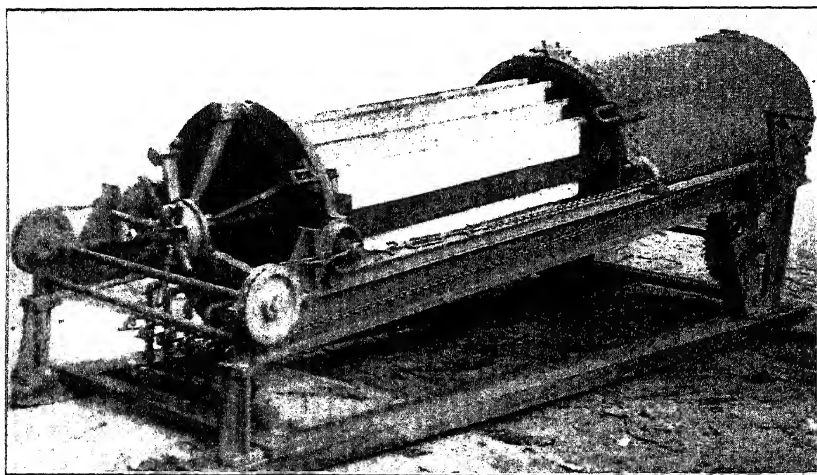


Fig. 80.   Kelly Filter Press.

**Drum Type Rotary Continuous Filters.** — This type of filter is best represented by the Oliver Filter and the Dorr Filter. The Oliver Filter is illustrated in Fig. 81. It shows a rotary drum revolving in an open tank. Tanks are generally made of steel

but under certain conditions are built of wood, cast-iron, concrete or steel plate covered with lead, copper, brass, monel metal, etc.

The drum shell is hollow, consisting of an outer porous surface which comprises the filter medium, and an inner supporting surface which is impervious to liquids or air. The space between the inner and outer surfaces of the shell is divided into com-
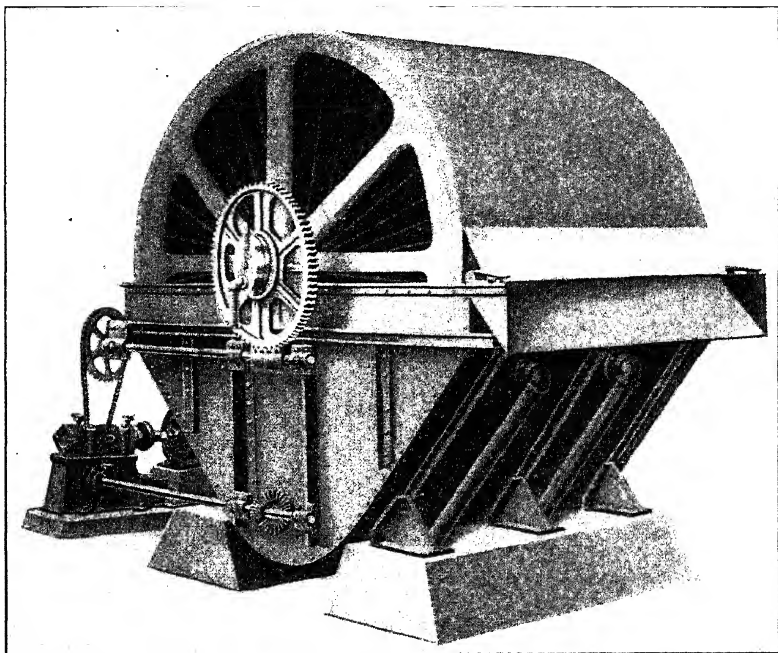


FIG. 81. Oliver Filter with Open Drum Heads and Paddle Agitator.

partments or sections by strips running parallel to the axis of the drum. The inner surface is covered with a grating which in turn carries the outer surface.

The filter medium is applied in one continuous piece around the drum and is held in place by wire windings on top of it around the drum. Each compartment is separate from the other and is connected by a system of piping to the automatic valve at the end of the shaft. This automatic valve controls the washing, drying, and discharging. The valve seat is bolted to the drum trunnion and revolves with it, the valve chamber being held in a fixed position.

In operating the Oliver Filter the material to be filtered is fed in a continuous stream to the open filter tank. The drum rotates and cake begins to form on the filtering surface which is under vacuum from the inside, as soon as it is immersed in the sludge. This continues until the drum emerges from the sludge. The filtrate passes through the cloth to the pipes, to the automatic valve and out, while the solids adhere to the filter surface of the drum, forming a cake. As soon as the liquid disappears from the cake, wash water is sprayed on and when washing is completed the vacuum is continued to dry the cake. Just before the cake reaches the scraper to discharge, compressed air replaces the vacuum and the cake is loosened and meets the scraper in this condition. The clean filter surface then enters the solution again for another cycle.

Figure 82 shows an installation layout of a vacuum filter and its accessories.
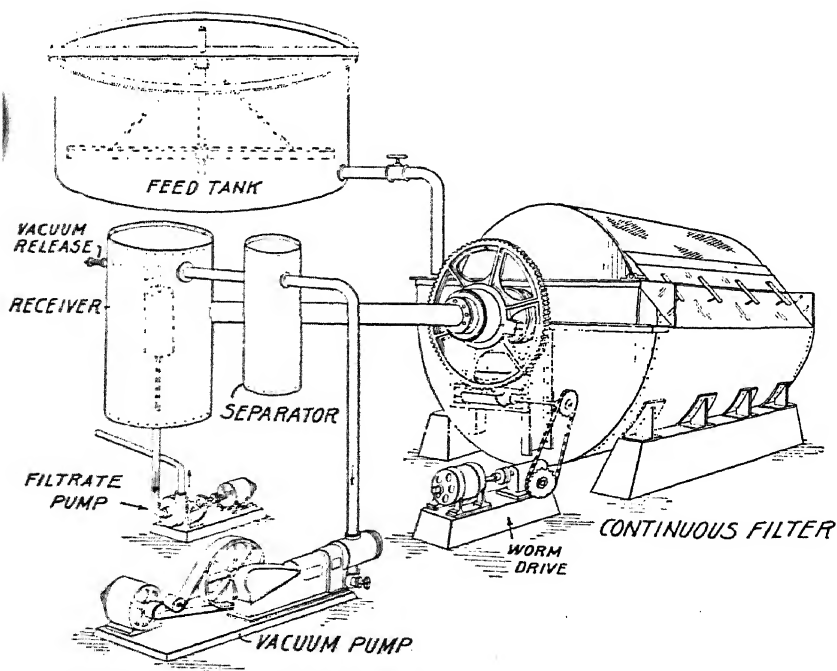


FIG. 82.    Installation Layout of a Vacuum Filter and Its Accessories.

The American Continuous Disc Filter. — This consists of a number of discs mounted on a horizontal shaft, the discs dipping into a tank below the shaft. The discs as shown in Fig. 83 are built up of sector-shaped units which are made of a rigid frame containing a double crimped wire body and having a projecting
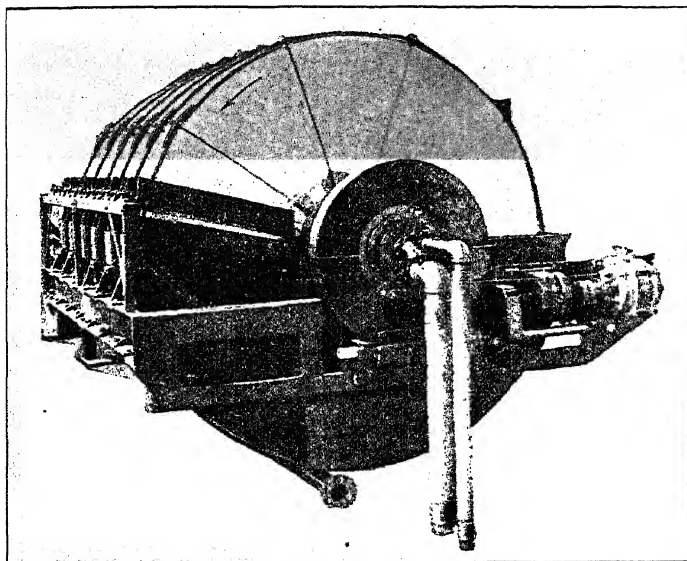


FIG. 83.   American Continuous Disc Filter.

nipple that enters the horizontal shaft.   Each sector is covered with a cloth bag properly fastened on.   A filtrate conduit in the sectionalized shaft drains all discs located in any given arc of rotation, and such discharge is controlled by the rotary valve at the end of the shaft.

One side of the tank, into which the discs dip, is continuous and common to all discs, while the other side has a number of separate extensions for the discharge of cake from each disc.   These extensions carry scrapers on their upper edges, which bear against the cloths slightly to scrape off the cake as the bags are inflated slightly by air.

The operation is as follows: the tank is filled to the desired point with the material to be filtered, the leaves are rotated. The leaves pick up cake from the sludge by means of the vacuum

on the inside of the sectors.   The filtrate passes through to the
shaft and out through the valve at the end of the shaft.   The
cake adheres to the outside of the discs and is washed by sprays
of water and then dried by the vacuum on the inside drawing
air through the discs.   When the discs reach the scrapers, com-
pressed air replaces vacuum on the inside of the sectors, thus
bulging the cloth slightly so that the cloths rub against the
scrapers and the cake is scraped off.   The disc then passes on
down to the sludge and the operation is repeated.   This filter
makes a good dewaterer.

**Dorrco Continuous Vacuum Filter.** — In this filter the filter
medium is applied to the inside of the drum and all the piping is
located on the outside of the drum so that the building and dis-
charging of the cake is opposite to that of other makes of con-
tinuous rotary filters.   The filter medium is divided into sections
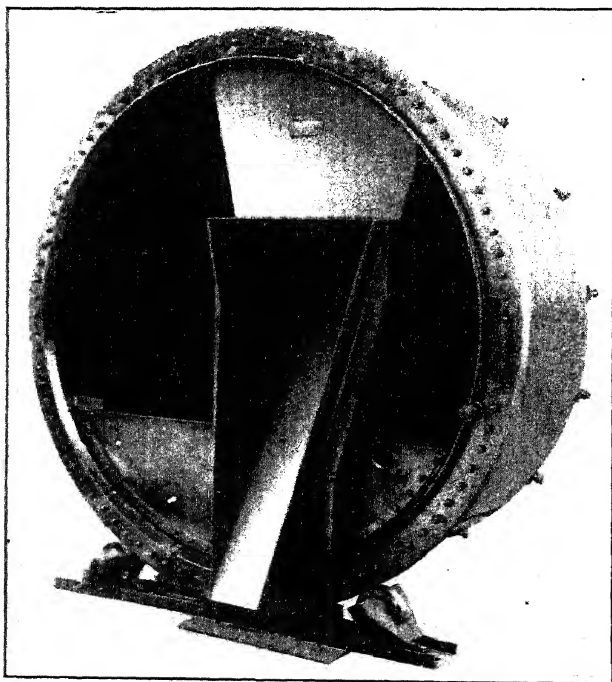


Fig. 84.   Open end with Discharge Hopper and Chute of Dorrco Continuous
Vacuum Filter.

or panels and is easily removed.    Through a port valve of the usual type adjacent to the closed end of the drum, vacuum for cake forming, drying and washing, as well as air for cake discharge, are applied to the panels.

At the open end of the drum, there is provided an internal flange by which the pulp is retained during filtration, thus eliminating the filter tank.

Figure 84 shows the open end of the filter with·the discharge hopper and chute.

Figure 85 shows the closed end with piping, etc.
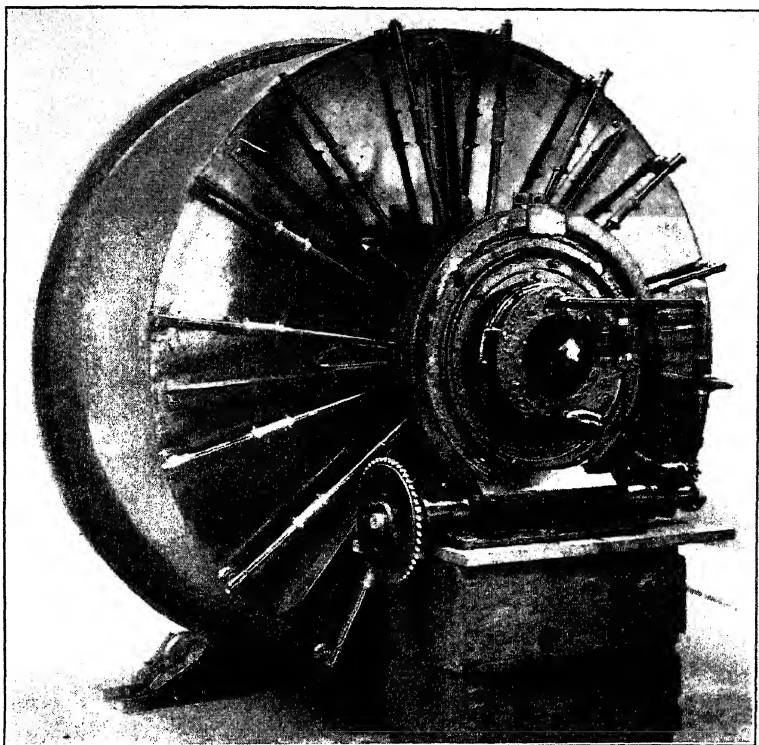


FIG. 85.   Closed end with Piping of Dorrco Continuous Vacuum Filter.

Figure 86 is a sketch showing the segregation of pulp in the filter.   This illustrates how gravity aids filtration by causing the larger particles to segregate against the filter medium.

**Vallez Rotary Pressure Filter.** — The Vallez Filter consists of a cast cylindrical shell, divided on the horizontal centerline into two halves. The filter element is made up of a hollow shaft, carrying the filter leaves which are circular. The shaft supports
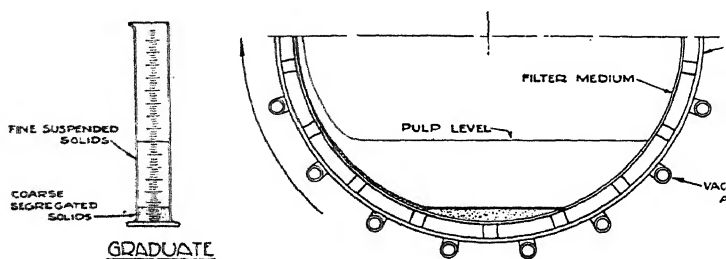


FIG. 86.  Sketch Showing Segregation of Pulp in Dorrco Filter.

the leaves, transmits the rotating drive and acts as a pipe to take the filtrate from the leaves and convey it out of the filter. A worm gear drive is located at one end, the other end being the discharge end for the filtrate. A spray pipe is located at the top of the upper half of the casing. Spray jets are located so that
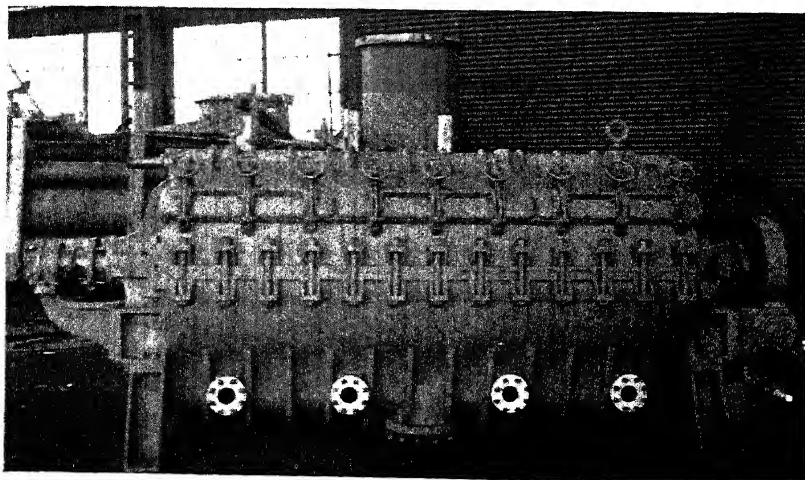


FIG. 87.  Vallez Filter Press.

the entire rotating filter surface is moistened when spraying the cake for cleaning it off the leaves.

The extreme bottom of the lower half of the shell is trough shaped and contains a right and left hand screw conveyor for carrying the cake to the center door in the bottom of the shell when discharging the cake after drying. If cake is to be sluiced out or a volatile solvent is used a large drain connection is used instead. A horizontal perforated pipe is used in the bottom of the shell for agitating the discharged cake with steam or air. Sight doors on the shell are used to examine the cake if needed.

The operation of the Vallez filter consists in closing the filter, filling with sludge, building the cake to the desired thickness, washing the cake if required, discharging the cake either dry or by sluicing.

Figure 87 shows the construction of the filter and Fig. 88 a sec-
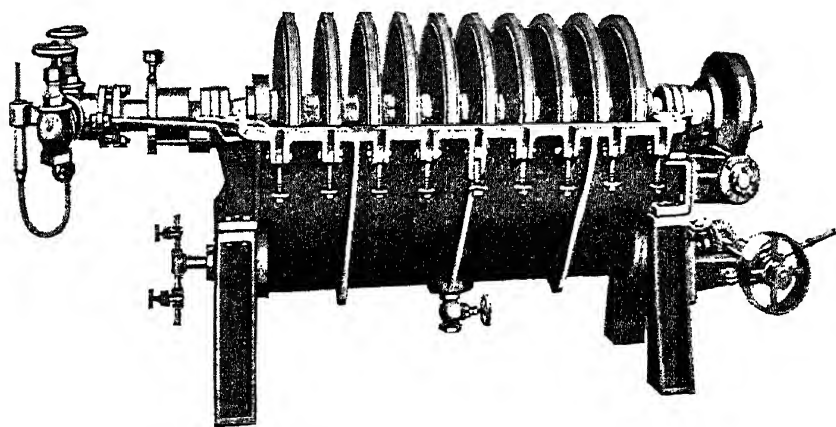


Fig. 88. Vallez Filter Press Open Showing Filter Leaves.

tional view, with the top half removed to show the leaves and the method of disintegrating the cake in case of sluicing.

# CHAPTER VIII

## DRYING

JOHN C. OLSEN, Ph.D., D.Sc.

Drying may be defined as the removal of a volatile liquid such as water from some other substance in which it may or may not be chemically held. The substance to be dried may be a gas, liquid, or solid. The methods employed are dependent upon the physical state of the substance to be dried.

**Drying of Gases.** — Gases are frequently dried by passing the moist gas over a dehydrating substance such as calcium chloride, calcium oxide, concentrated sulfuric acid or phosphorous pentoxide. The water may also be absorbed by a solid such as silica gel. Calcium chloride is very commonly used because it can conveniently be prepared in solid granular form very well adapted for use in trays over which the gas to be dried is passed. The calcium chloride dissolves in the absorbed water and the solution drips through the trays to a suitable receiver from which it can be readily removed. The water may be removed from the solution by heating and the dried calcium chloride granulated and used again. As the vapor tension of the water combined with calcium chloride increases rapidly with increase in temperature, calcium chloride cannot be used to dry gases at high temperature.

*Concentrated sulfuric acid* is a very much better dehydrating agent than calcium chloride and may also be used at higher temperatures. As it is a liquid, the gas must either bubble through it or towers must be used which are constructed of acid resisting material such as lead, silica, coke, etc. The gas to be dried must be introduced at the bottom of the tower while the acid flows down the tower. After use, the diluted acid may be concentrated, or used in operations where dilute acid is required.

*Calcium oxide* is a less effective dehydrating agent than calcium chloride and also absorbs acid gases. Being a solid it is used in the same manner as calcium chloride but it is not advantageous to dehydrate it for repeated use.

244

*Phosphorous pentoxide* is the most efficient dehydrating agent, the vapor tension of water which it has absorbed being less than that in sulphuric acid. On account of its high cost, it is seldom used.

*Refrigeration.* — Another method of drying gases which is often used involves refrigeration. The temperature of a gas may be reduced to a point at which the vapor tension of water is as small as, or smaller than, the vapor tension of water over the dehydrating substances used such as calcium chloride and sulphuric acid. At these low temperatures the water vapor will condense to liquid or solid, leaving the gas dry. The gas may be cooled by the usual ammonia or other refrigerating system.

**Drying of Liquids.** — If water is present in liquids in small amounts, it may be removed by drying which is often done by bringing the liquid into contact with substances which are insoluble in the liquid and which will absorb water. Calcium chloride is often found to answer these requirements.

If large amounts of water are present with other liquids, separation is generally effected by distillation.

**Drying of Solids.** — The most common problem met with in drying is the removal of water or other volatile liquid from a solid material. The water is first vaporized, the necessary heat being supplied by one of several methods. The water vapor must be removed as rapidly as formed. A study of methods of drying will involve both methods of heating the material to be dried and also methods of removing the water vapor formed. A study must also be made of methods of handling the material and transmitting heat to it.

**Free and Hygroscopic Moisture.** — Water seems to exist in most materials in two forms, commonly known as " free moisture" and "hygroscopic moisture." The free moisture during evaporation follows the laws of uncombined water. The hygroscopic water is probably adsorbed or loosely combined with the solid substance. The amount of hygroscopic water present is a function of the temperature and humidity of the air in contact with the substance. For instance, cotton will hold 6 per cent of moisture at ordinary temperatures in air at 50 per cent humidity. Cotton containing more than 6 per cent water will lose moisture

in contact with air of 50 per cent humidity, while cotton containing less than 6 per cent water will gain moisture in contact with such air.   It is obvious that the vapor tension of adsorbed water is very much less than that of free moisture.   Free moisture will evaporate in contact with unsaturated air.   Wood, leather, soap, textiles, etc., hold hygroscopic moisture.   In many cases it is not desirable to remove the hygroscopic moisture or only a portion of it so that the drying operation is concerned mainly with the removal of the free moisture.

**Transmission of Heat.** — Heat in transmitted to boiling liquids mainly by convection, the portion of the liquid which becomes heated by contact with the heating surface being displaced by colder liquid which has been out of contact with the hot surface.   Bubbles of steam are also formed at the hot surfaces and quickly pass up through the liquid and are carried away.

Convection currents are set up as a result of the difference in density between the hot and cold portions of the liquid.   When a liquid is heated it invariably increases in volume, and its density decreases.   Hence this portion tends to rise and causes circulation of the liquid by convection.

Heat can be transmitted through a solid only by conduction. The conductivity of solids is generally very low.   Even with the highest conductivity, this method of transmitting heat is very much slower than by convection.   The transmission of heat in well designed evaporators ranges from several hundred to a thousand B.t.u. per square foot per hour per degree temperature difference.   Driers handling solid material may not show a heat transmission of more than a few B.t.u. per hour per degree.

**Rate of Diffusion.** — Evaporation of water from solid material generally takes place at the surface only.   The moisture in the interior of the lump must diffuse to the surface.   This is also a very slow process.   The rate of diffusion varies a good deal with the character of the material when moist and also with the condition of the dried material.   This may form a more or less hard impervious crust.   It is for this reason that the drying rate varies very greatly with the thickness of the layer of solid material being dried.   Thinner layers may dry very much more rapidly than thicker layers.

**Rate of Drying.** — The drying rate is also different for free moisture and for hygroscopic or adsorbed moisture. Materials differ very much as to their affinity for moisture.

If a given temperature is maintained the rate of drying will depend upon two factors: (1) the rate at which the water evaporates; and (2) the rate at which the water vapor or other volatile constituent is removed. The evaporation rate is generally the slower of the two and determines the rate of drying.

**Deliquefaction.** — The process of drying is often preceded by another process of dewatering such as evaporation or filtration or both of these. The entire operation may be described as dewatering or the more general term deliquefaction, which would include the removal of other liquids as well as water, may be used.

Mechanical deliquefaction, as by filtering, is always a cheaper process, when it can be applied, than is deliquefaction by adding heat. One possible exception to this general rule is where there is waste heat available at little or no cost for utilization. Frequently the characteristics of the material being processed predetermine which method of deliquefaction should be used. Most such problems, however, are solved by a combination of the two methods, evaporating to the maximum concentration that can be handled in the drier.

The methods of deliquefaction may be classified as follows:

*I. Purely Mechanical*
    (By pressure methods
      such as Filters)

*II. Physical Change*
    (By addition of heat)
      *A.* Stills
      *B.* Evaporators
      *C.* Driers

*Driers*

Classified by
  *A.* Method of Application of Heat
  *B.* Type of Design

*A. Driers* utilizing various methods of application of heat
    1. Radiant Heat Driers
        (*a*) Solar such as salt crystallizer
        (*b*) Furnace fired [1]
        (*c*) Electric

[1] Frequently termed Direct Fired.

2. Direct Fired Driers
   (*a*) No utilization of Flue Gases
   (*b*) Circulation of Flue Gases
   (*c*) Partial or complete recirculation of Flue
       Gases
3. Indirect Fired Driers
   (*a*) Single Heating Medium
       1. Steam
       2. Circulating Oil,
           Mercury Vapor,
           Electricity
       3. Air
           Inert Gas
   (*b*) Multiple Heating Media Driers
       1. Steam — Air

B. *Driers* of various types of design
   4. Batch Process Driers
      (*a*) Dry Rooms
      (*b*) Vacuum Drying Rooms
      (*c*) Rotary Driers
          1. Atmospheric [2]
          2. Vacuum [2]
   5. Continuous Driers
      (*a*) Tunnel Driers
          1. Horizontal
          2. Vertical
          3. Involved Path [3]
      (*b*) Drum Driers
      (*c*) Spray Driers

**Removal of Water Vapor.** — Two general methods are in use
for removal of the water vapor.  One method consists in passing
a current of warm dry air, or other gas which is chemically inert
to the substance being dried, over the material to be dried.  The
second method uses the so called vacuum drier which consists of
a  closed  chamber  connected  with  a  condenser  and  vacuum

[2] Vacuum sometime operable as semi-continuous; atmospheric operable either as
semi-continuous or fully continuous.

[3] Such as textile driers, where the goods are carried progressively forward in a
serpentine path.

pump. A clear understanding of either of these methods requires a study of the vapor tension of water or other liquid which must be removed. As water is the most common liquid to be removed by drying, the principles involved will be presented with reference to this liquid.

**Vapor Tensions.** — When water is confined in a vessel, it will evaporate until the vessel contains that amount of water vapor which will produce a given gas pressure which is a constant for a definite temperature and independent of the presence of air or other gases in the vessel, provided no chemical reaction takes place with the water vapor. If the temperature is raised, more molecules of water will pass into the vapor state until a new pressure is reached which is a constant for the new temperature. If, on the contrary, the temperature is decreased, some of the molecules in the vapor state will pass into the liquid state or condense until a pressure is reached corresponding to the new temperature. The following table gives the vapor pressures corresponding to temperatures of − 50° to 100° C.

VAPOR TENSION OF WATER IN MILLIMETERS OF MERCURY

| °C. | Mm. of Mercury | | °C. | Mm. Mercury | °C. | Mm. Mercury |
|-----|------|-------|-----|-------------|-----|-------------|
| | Ice | Water | | | | |
| −50° | .034 | | 5 | 6.528 | 50 | 92.17 |
| −40° | .105 | | 10 | 9.179 | 55 | 117.77 |
| −30° | .292 | | 15 | 12.728 | 60 | 149.21 |
| −20° | .787 | .960 | 20 | 17.406 | 65 | 187.51 |
| −15° | 1.257 | 1.451 | 25 | 23.546 | 70 | 233.8 |
| −10° | 1.974 | 2.159 | 30 | 31.555 | 75 | 289.32 |
| −5° | 3.032 | 3.167 | 35 | 41.853 | 80 | 355.47 |
| 0° | 4.579 | 4.579 | 40 | 55.341 | 85 | 433.79 |
| | | | 45 | 71.90 | 90 | 526.00 |
| | | | | | 95 | 634.01 |
| | | | | | 100 | 760.00 |

It will be noted from this table that water will pass directly from the solid to the vapor state, that is, ice will evaporate. The rate of evaporation from liquid water is considerably greater than from ice. Inspection of the table will also show that the evaporation of water will increase rapidly with rising tempera-

ture and that it would be advantageous to carry out drying operations at relatively high temperatures.

When water passes into the vapor state, heat is absorbed, the exact amount for a given temperature being given in table in the appendix.   This amount of heat must be supplied in order to maintain the drying process.

**Rate of Drying.** — In many cases the temperature to which the drying material is subjected as well as the rate of evaporation must be regulated with the greatest care.   Some substances such as milk, eggs, fruit, etc. can be dried only at relatively low temperatures in order to retain their flavor, solubility, color, etc. Many crystalline substances lose their water of crystallization if overheated.   In some cases a substance will dry at the surface while the interior portions remain moist.   As drying generally results in shrinkage, this surface drying frequently results in cracking of the surface.   This is particularly true with reference to lumber.   When dried too rapidly, the surface cracks so that the material is greatly injured.   To overcome this difficulty, the lumber must be dried at a rate such that the diffusion of moisture from the interior to the surface may take place as rapidly as the loss of moisture from the surface.   In order to accomplish this, it is necessary not only to regulate the temperature but also to maintain a minimum vapor tension of the moisture in the air in contact with the surface.   For many substances of this character 80 per cent humidity is required.   This results in a retardation of the drying, but the shrinkage is uniform and no cracking of the surface results.   Many colloidal substances must be dried under similar conditions in order to avoid the formation of a crust on the surface.   In some cases, material of this kind can be cut into thin sheets and the drying greatly accelerated.   In some cases it may be desirable to produce a surface crust in order to handle the material more advantageously.

A great many substances which must be dried by the chemical engineer do not require such careful regulation of the rate of drying, the only requirement being that a given maximum temperature shall not be exceeded.

At a given temperature, evaporation will proceed until the limiting pressure of water vapor for that temperature is reached. Evaporation will then cease because as much water vapor will condense as evaporates.   In order that evaporation shall proceed,

it is necessary to remove the water vapor as rapidly as it is formed. This is accomplished in general by either vacuum or air drying.

**Vacuum Drying.** — In vacuum drying the material to be dried is confined in an air tight place, means of heating is provided, and a vacuum is produced by means of an air pump. A condenser must usually be provided for condensation of the water or other volatile liquid. It is installed between the drier and air pump. As the boiling point of water is reduced by the vacuum, drying takes place at extremely low temperatures, 75 to 100° F. being obtained in commerical practice. This is one of the advantages of vacuum drying by which materials such as organic and food products which are sensitive to overheating may be successfully dried.

As air is excluded, oxdation is prevented. This also eliminates possible contamination with impurities which may be present in the air. The drying operation is also independent of variations in the moisture content and temperature of the air.

A volatile solvent can be readily recovered in vacuum drying as the vapor is not diluted with air and therefore can be readily condensed.

While in many cases vacuum drying is the best method for drying the material at hand, in other cases it is not at all suitable. Vacuum chamber driers or dry rooms are always operated on the batch system and continuous operation is not possible. When large amounts of material must be handled economically, a continuous process must be used. In other cases where high temperatures may be employed without injury to the product the low temperatures of vacuum drying are not advantageous. Where high temperatures must be employed to obtain a satisfactory product, vacuum drying is usually not advantageous.

**Vacuum Shelf Drier.** — This apparatus (Fig. 89) consists of an air-tight chamber fitted with a door which can be closed air-tight. The chamber is constructed either of welded or riveted steel or of cast iron. The doors are usually of cast iron hinged and provided with heavy fasteners. A heavy molded rubber gasket is provided to give a gas-tight joint when the door is closed. The shelves upon which the material to be dried is placed are constructed hollow of welded sheet steel. Steam, hot water or hot oil is circulated through these shelves in order to heat the

ture and that it would be advantageous to carry out drying operations at relatively high temperatures.

When water passes into the vapor state, heat is absorbed, the exact amount for a given temperature being given in table in the appendix. This amount of heat must be supplied in order to maintain the drying process.

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As air is excluded, oxdation is prevented. This also eliminates possible contamination with impurities which may be present in the air. The drying operation is also independent of variations in the moisture content and temperature of the air.

A volatile solvent can be readily recovered in vacuum drying as the vapor is not diluted with air and therefore can be readily condensed.

While in many cases vacuum drying is the best method for drying the material at hand, in other cases it is not at all suitable. Vacuum chamber driers or dry rooms are always operated on the batch system and continuous operation is not possible. When large amounts of material must be handled economically, a continuous process must be used. In other cases where high temperatures may be employed without injury to the product the low temperatures of vacuum drying are not advantageous. Where high temperatures must be employed to obtain a satisfactory product, vacuum drying is usually not advantageous.

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drying material which is generally placed in flat shallow pans or trays which are placed on the hot shelves. The heat must be transmitted through the pans into the material being dried. It is essential that both pans and shelves be as flat and even as possible in order to secure satisfactory transmission of heat which can be transmitted only by conduction. Transmission of heat through a vacuum is very slow. On the other hand the
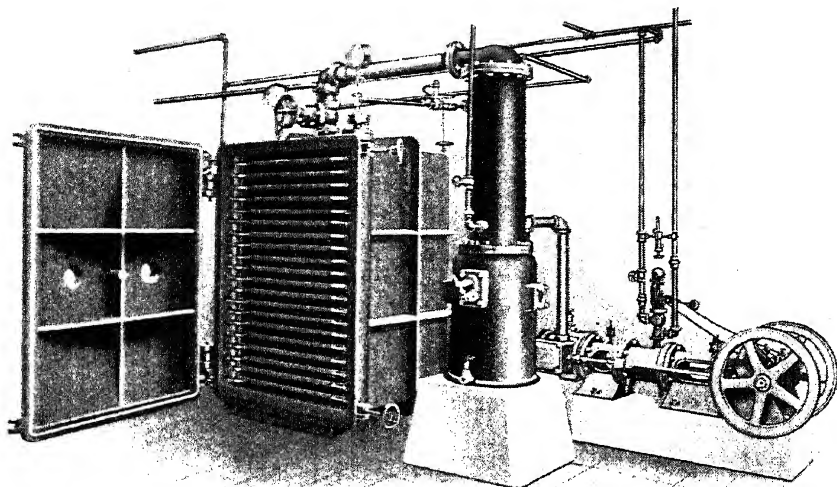


FIG. 89. Vacuum Shelf Drier Installation with Surface Condenser and Dry Vacuum Pump.

low temperature at which drying takes place in a vacuum gives a relatively high temperature difference. Considerable labor is required for loading and unloading trays and charging and discharging the drier. If the drier is properly insulated the heat losses are low, the vacuum drier operating at a high thermal efficiency. Steam consumption usually amounts to about 1.25 pounds per pound of water evaporated.

*Operating Expense.* — On account of the large volume of the vapor and its high velocity, surface condensers must be installed of large volume. If the solvent must be recovered, surface condensers must be used. The following table [4] gives the method of calculating the operating expense of drying a given material

[4] This and the two following tables are quoted from article by Chas. O. Lovett and D. J. Van Marle. Jour. of Ind. & Eng. Chem., **13**, 600.

which in this case was rubber. Interest on the investment or depreciation of equipment is not included in this table. These items must be added to get the total cost.

Floor space of equipment, including working space.................304 sq. ft.
Duration of test............................................... 3 hrs.
Steam pressure................................................ 3 lbs.
Vacuum....................................................... 27.1 in.
Temperature of rubber at start................................118° F.
Temperature of rubber at finish...............................180° F.
Percentage of moisture evaporated............................. 17.7
Weight of dry rubber..........................................740 lbs.
Steam consumption per lb. of water evaporated..................... 1.2 lbs.
Weight of dry rubber per sq. ft. pan surface...................... 1.3 lbs.
Steam consumption per lb. of dry rubber.......................... 0.259 lb.
H.p. of vacuum pump........................................... 9.25

*Cost*

192 lbs. of steam at 40 cts. per 1000 lbs.....................$0.0768
20.712 k.w. hrs. at 1.5 cts. per k.w. hr....................... 0.3107
690 gal. of water at 6 cts. per 1000 gal....................... 0.0414
                                                                ———————
                                                                $0.4289

*Labor*

Filling pans..................................................$0.7600
Loading drier ................................................ 0.1748
Unloading drier .............................................. 0.1122
Emptying pans................................................. 0.6068
                                                                ———————
    Total cost of labor......................................$1.6538
                                                                ———————
    Total....................................................$2.0827

Cost per lb. of dry rubber....................................$0.002814
Cost per ton of dry rubber.................................... 5.628

**Vacuum Rotary Drier.** — Where it is necessary or possible to agitate the material to be dried, it is advantageous to employ a rotary drier. These driers consist of a jacketed cylinder through the entire length of which a shaft is extended on which the agitator is mounted. Frequently the shaft is constructed as a heating tube. The material being dried comes into contact with the heated cylinder as well as the central tube. The constant agitation continually brings fresh material into contact with the hot surfaces. This results in better heat transmission than in the shelf drier.

All substances cannot be handled in rotary driers. Some form large lumps which retain the moisture tenaciously, while others tend to form a coating on the heating surfaces which interferes with heat transmission.

*Cost of Drying.* — Where this method is applicable, the cost of drying is lower than in shelf driers as may be seen from the following table:

| | |
|---|---|
| Duration of test............................................... | 4.87 hrs. |
| Steam pressure................................................ | 18.15 lbs. |
| Vacuum....................................................... | 27.05 in. |
| Size of drier .................................................. | 5×30 ft. |
| Weight of dry rubber.......................................... | 2994 lbs. |
| Percentage of moisture removed................................ | 46.6 |
| Steam consumption per lb. of water removed.................... | 1.14 lbs. |
| Steam consumption per lb. dry rubber.......................... | 1.001 lbs. |
| Power required for vacuum pump............................... | 9.43 h.p. |
| Power required for drier ....................................... | 9.50 h.p. |
| Floor space of equipment including working space............... | 540 sq. ft. |

*Cost*

| | |
|---|---|
| 2997 lbs. of steam at 40 cts. per 1000 lbs.................... | $1.199 |
| 10,800 gal. water at 6 cts. per 1000 gal..................... | 0.648 |
| 66.97 k.w. hrs. at 1.5 cts. per hr........................... | 1.005 |
| 0.8 hr. supervision at 40 cts. per hr........................ | 0.320 |
| 1.0 hr. loading and unloading at 40 cts. per hr............. | 0.400 |
| | |
| Total........................................................ | $3.572 |
| | |
| Cost per lb. of dry rubber.................................... | $0.001193 |
| Cost per ton of dry rubber................................... | 2.386 |

**Vacuum Drum Drier.** — This form of apparatus is designed for the dehydration of solutions from which solid material may be obtained by drying. The apparatus consists of a heated drum upon which the liquid is caused to flow in a thin layer. The drum revolves in a casing in which a vacuum is maintained. The speed of rotation of the drum must be so regulated that the solution is evaporated in less than one revolution. The solid is removed by a knife which is adjusted to scrape the drum. The dried material is removed by a suitable conveyor.

Various devices are employed to apply the liquid to the drum in a thin film. In every case it is desirable to utilize as large a proportion of the surface of the drum for drying as possible. For this reason the scraper which removes the solid material is

placed as near as possible to the point at which the liquid to be dried is applied to the drum.

*Film drying* is very efficient and economical because heat transmission to a liquid is much more rapid than to solids. As the liquid evaporates at a low temperature in a vacuum the temperature difference is large. The rate of evaporation in this type of driers frequently reaches 5 pounds or more of water per square foot of heating surface per hour. On account of the short time during which the liquid is in contact with the heated
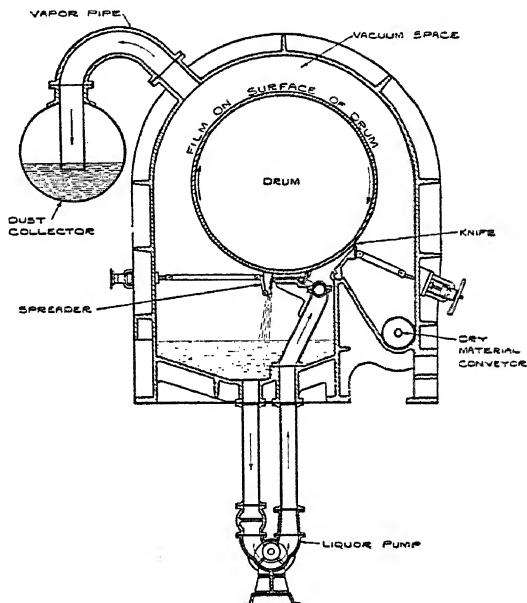


FIG. 90. Sectional View, Vacuum Drum Drier

surface, this type of drier is especially suited to the drying of substances which are sensitive to heat such as milk, eggs, medicinal extracts, and other organic substances.

*Continuous Drying.* — The drying may be made continuous by installing two receivers which are operated alternately. When one receiver has been filled, the opening into the drying chamber is closed by means of a valve and the receiver is emptied. During this operation the dried material is conveyed to the other receiver. A small vacuum pump is installed for evacuating a

receiver before it is connected to the drying chamber after being emptied. The moisture content of the dried material may be controlled by varying the steam pressure, speed of the drum, or the thickness of the film.
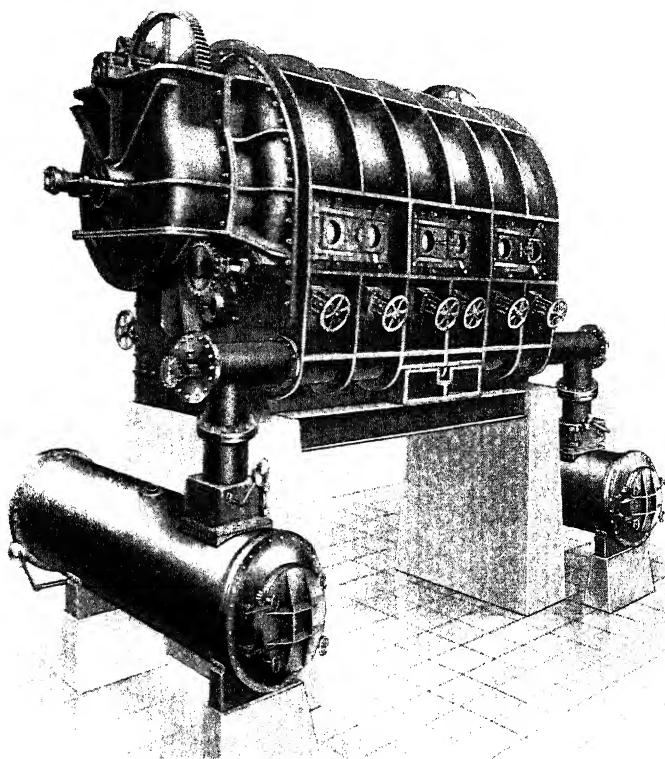
FIG. 91.   Vacuum Drum Drier.

Various devices are used for applying the liquid to be dried to the drum. A reservoir may be placed beneath the drum which collects some of the liquid by direct contact with it. In other cases a small roll is installed between the drum and the tank holding the liquid. In some cases an adjustable spreader bar is installed so that the thickness of the film may be accurately regulated.

In the double drum type the liquid is applied between two heated drums revolving in opposite directions. The liquid is forced between the drums and the dried material is scraped off in the upper quarter of the revolution.

*Operating Expense.* — The running expense of drying sulfite waste liquor by continuous vacuum drying is given in the following table:

| | |
|---|---|
| Size of drum | 5×12 ft. |
| Steam pressure | 39 lbs. |
| Vacuum | 27.8 in. |
| Speed of drum | 8.25 r.p.m. |
| Drying time | 7.27 sec. |
| Duration of test | 4 hrs. |
| Weight of liquor, 31.9° Bé. at 60° F. | 8011.00 lbs. |
| Weight of dry material | 4483.00 lbs. |
| Weight of dry material per hr. | 1120.75 lbs. |
| Moisture in solution | 47.83 per cent |
| Moisture in dry material | 6.76 per cent |
| Steam consumption per lb. water evaporated | 1.165 lbs. |
| Steam consumption per lb. dry material | 0.917 lb. |
| H.p. of drum, pumps and conveyor | 30.16 |
| Supervision | 1 man |
| Floor space of equipment including working space | 797 sq. ft. |

### Cost

| | |
|---|---|
| 4112 lbs. of steam for drying at 40 cts. per 1000 lbs. | $1.6448 |
| 4102 lbs. of steam for power at 40 cts. per 1000 lbs. | 1.6408 |
| 12,700 gal. water for condenser at 6 cts. per 1000 gal. | 0.7620 |
| 4 hrs. labor at 40 cts. per hr. | 1.6000 |
| Total | $5.6476 |
| Cost per pound of dry material | 0.001259 |
| Cost per ton of dry material | 2.518 |

Using motor driven equipment the cost would be:

| | |
|---|---|
| 4112 lbs. of steam at 40 cts. per 1000 lbs. | $1.6448 |
| 12,700 gal. water at 6 cts. per 1000 gal. | 0.7620 |
| 90 k.w. hrs. at 1.5 cts. per k.w. hr. | 1.3500 |
| 4 hrs. labor at 40 cts. per hr. | 1.6000 |
| Total | $5.3568 |
| Cost per lb. of dry material | $0.001195 |
| Cost per ton of dry material | 2.390 |

**Air Drying.** — In this method of drying, a current of heated air is passed over the material to be dried. The heated air serves two purposes. It carries away the water vapor formed

during drying and also furnishes the heat required to maintain the evaporation. These two processes take place simultaneously provided the air used for drying is not saturated with water vapor. Saturated air is in equilibrium with a moist surface provided there is no change in temperature. When warm air which is not saturated with water vapor is in contact with a moist surface, water vapor will be given off until the air is saturated, the heat required to evaporate the water being furnished mainly by the air. Therefore, the temperature of the air and the moist surface will be lowered, equilibrium being reached when the air is saturated with water vapor. This temperature which may be called the *temperature of evaporation* may be calculated from the latent heat and specific heat of the saturated vapor, the specific heat and density of the atmosphere, and the degree of initial saturation of the atmosphere with the vapor. This temperature is identical with the wet bulb temperature of the air. In other words, when air is used for drying and all of the heat is furnished by the air, then when the air is saturated with moisture its temperature will be the wet bulb temperature of the air in its initial condition. The latent heat of the water evaporated will be found to be exactly equal to the loss in sensible heat of the air.

*Rate of Drying.* — The same relation holds for any liquid which evaporates in the air and may be expressed by the following formulae:

Let $W_1 =$ the initial weight of vapor content per lb. of vapor free air,

$W_2 =$ weight of vapor taken up by air,

$t =$ temperature of the air,

$a =$ specific heat of air,

$v =$ specific heat of the vapor,

$r =$ latent heat of evaporation of the liquid.

As the heat absorbed as latent heat of evaporation is equal to the loss in sensible heat of the air we have:

$$vdw = (a + w_1 v)dt.$$

Integrating between the limits $W_1$ and $W_2$ and $t_1$ and $t_2$ we obtain:

$$(W_2 - W_1) = (a + W_1 v)(t_2 - t_1).$$

As $r(W_2 - W_1)$ represents the amount of heat used up in evaporation and $a$ and $w_1v$ are constants, the rate of evaporation must be proportional to $t_2 - t_1$  As $t_2$ represents the initial temperature of the air and $t_1$ is the temperature of the drying material which is always equal to the wet bulb temperature of the air, the rate of drying must be proportional to the difference between these temperatures which is known as the *wet bulb depression*.

As the wet bulb depression is proportional to the difference in vapor tension at the two temperatures the rate of evaporation is also proportional to the difference in vapor tension of the volatile liquid in the dry and moist air.

Taking the weight of 1 cu. ft. of air at 60° F. at 0.0761 lb. and the specific heat of air at constant pressure as 0.2375 the amount of heat needed to raise 1 cu. ft. of air 1° F. will be 0.01807 B.t.u. (0.0761 × 0.2375).   One cu. ft. of air dropping 1° F. in temperature will release 0.01807 B.t.u.

The latent heat of evaporation of water varies with the temperature.   At 60° F. it is 1058 B.t.u.   Therefore the heat liberated by one cu. ft. of air dropping 1° F. below 60° will evaporate (.01807/1058) = .000017 lb. of water.   This continues until the air is saturated with water vapor when the temperature will be the wet bulb temperature.

*Drying Capacity of Air.* — It follows from this that the drying capacity of the air is a function of the so-called wet bulb depression, that is, the difference between the dry and wet bulb temperature of the air.   This difference is increased by heating the air or taking moisture out of it.   It also decreases as evaporation takes place, becoming zero when the air is saturated. In practice it is not found possible to operate so that the air becomes completely saturated with water.   In the illustration given if the wet bulb depression was 10° F. the amount of water evaporated by one cu. ft. of air would be .00017 lb.

The *rate of evaporation* is also proportional to the difference in vapor tension of the moisture in the material being dried and the vapor tension of the moisture in the drying air.   The vapor tension of the moisture in the material is a function of the temperature and also of the condition of the water as to whether it is free and present at the surface in sufficient quantity to evaporate freely, or adsorbed.   The vapor tension of the moisture in the air may be determined by obtaining the dew point temperature.

The wet bulb depression of the air is dependent upon the vapor tension of the moisture and the temperature of the air.

The vapor tension of water in air may be calculated from the dry and wet bulb temperatures as follows:

$f$ = vapor tension of water in the air in inches of mercury,

$f'$ = maximum vapor tension of water at the wet bulb temperature $t'$,

$t$ = dry bulb temperature in °F.,

$t'$ = wet bulb temperature in °F.,

$P$ = barometric pressure in inches of mercury,

$$f = f' - 0.000367\, P(t - t') \left( 1 + \frac{t' - 32}{1571} \right).$$

If $F$ is the maximum vapor tension of water at the dry bulb temperature then the relative humidity is $f/F$.

*Velocity of Air.* — During the drying of a moist material, a layer of water vapor or a mixture of air and water vapor is formed on the surface of the material. If the air in contact with the material is still, the water vapor must diffuse into this air. The rate of diffusion determines the rate of drying, so far as the air is concerned. On the side of the material being dried, the rate of drying is determined by the rate at which the moisture diffuses to the surface of the solid. If the air is in motion, the layer of water vapor near the surface of the material will be carried away resulting in increased evaporation. The rate of evaporation is therefore influenced by the velocity of the air current. It has been found that the influence of an air current parallel to the surface is not the same as that of a current perpendicular to the surface.

If $e$ and $e'$ represent the vapor tension of the moisture in the air and over the material, $w$ = water evaporated and $t$ = time, then the rate of evaporation may be represented by

$$\frac{dw}{dt} = x(e' - e).$$

$x$ varies directly as the molecular weight of the substance evaporating.

As the rate of evaporation increases with the velocity, if $a$ = rate of evaporation in still air and $b$ = rate of increase with

velocity, then

$$\frac{dw}{dt} = (a \times bv)(e' - e).$$

For example for water evaporating in still atmosphere, $R = 0.093$ $(e' - e)$, $R$ being the pounds of water evaporated per square foot per hour. In terms of heat units $H = 97$ $(e' - e)$, $H$ being the B.t.u. per square foot per hour.

For a current of air parallel to a horizontal surface

$$W = 0.093 \left( 1 \times \frac{v}{230} \right) (e' - e),$$

where $W =$ lbs. evaporated per sq. ft. per hour; $v =$ velocity of air over surface in ft. per min. That is at a velocity of 230 ft. per minute the evaporation is twice that in still air while at 460 ft. the evaporation is three times as much.

In terms of heat units the following expression holds:

$$H = 97 \left( 1 + \frac{v}{230} \right) (e' - e).$$

With an air current perpendicular to the surface the rate of evaporation is nearly double.

*Wet Bulb Depression.* — As the drying capacity of the air is proportional to the wet bulb depression, it is desirable to secure the greatest possible difference between the wet and dry bulb temperatures. If either one of these temperatures is fixed, the greatest possible wet bulb depression will be obtained with absolutely dry air which as is well known has the greatest ability to evaporate and absorb moisture.

Figure 92 gives three curves showing the vapor tension and maximum moisture absorbing capacity of air having a given wet bulb temperature. Curve I gives the grains of moisture per pound of dry air of air having a given wet bulb temperature. Curve III gives the vapor tension of the moisture in the same air. Curve II gives the maximum dry bulb temperature of air having a given wet bulb temperature. This is the temperature of absolutely dry air which will have a given wet bulb temperature. Ordinary air containing some moisture will have a maximum dry bulb temperature somewhat less than this.

For instance, absolutely dry air having a temperature of 280° F. will have a wet bulb temperature of 100°. This would give a

useful temperature drop of 180°.   This air could evaporate and
absorb 300 grains of moisture per pound of dry air while dropping
in temperature from 280 to 100° F.   The amount of moisture
which air containing some moisture but having a wet bulb tem-
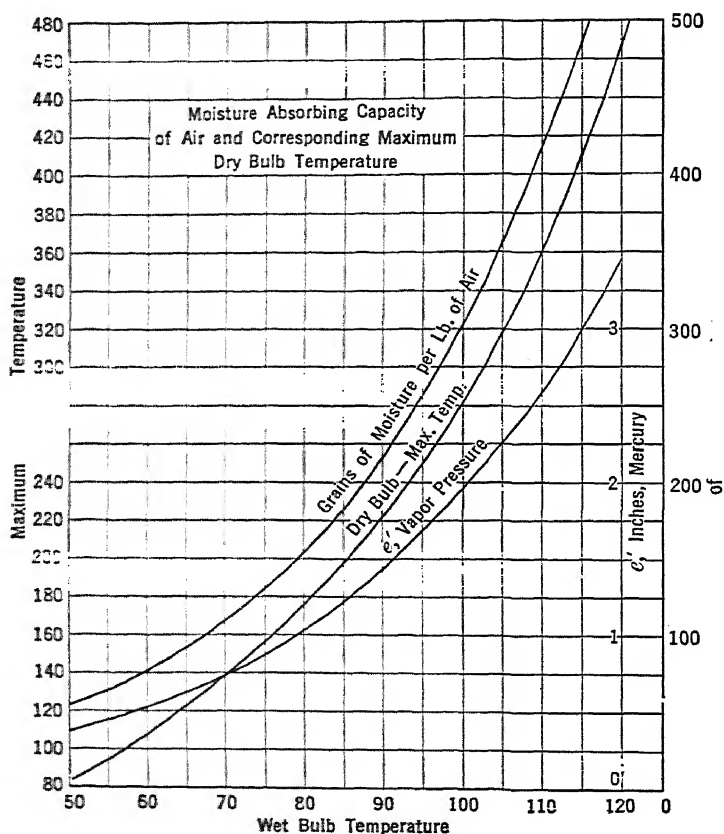


FIG. 92.

perature of 100° is obtained by subtracting the initial moisture
content in grains per pound of dry air from 300.

  *Reheating Air.* — Air containing a given amount of moisture
heated to a definite temperature is capable of taking up a definite
amount of moisture, the temperature dropping in the process to a
minimum which is the wet bulb temperature.   On reheating and
circulating this air over the moist material, it is capable of taking

up an additional amount of moisture. In doing so it will again drop to a new wet bulb temperature which is higher than the first wet bulb temperature. In this manner it is possible by reheating and recirculating to raise the temperature and moisture content of the air to any given desired point. In the operation of driers it is customary to reheat and recirculate the air only a portion of which is fresh air; the moisture-laden hot air being discharged at the temperature and humidity desired.

*Dehydrating Air.* — It has also been found feasible to remove the moisture from the air, before recirculating, by means of cooling coils or by means of a spray of cold water. The air must be reheated before it can again be used for drying. It is also possible to use a water absorbant such as silica gel which will absorb a large amount of water from moist air. The water is expelled from the silica gel by means of heat after which it can be used again. It will reduce the moisture content of the air to a very low point. The air from which the moisture is absorbed becomes heated as the heat of absorption is exactly equal to the heat of evaporation.

*Amount of Air Required.* — In order to ascertain the amount of air necessary to dry a given amount of material, the following information will be needed: The percentage of water in the moist material and the percentage of water remaining in the final product. This is ascertained by laboratory experiments. The maximum temperature at which drying may be carried out is also ascertained by a study of the material to be dried. This involves a study of the temperature at which decomposition takes place and also a study of the factors which influence speed of drying. In some cases fusion of a substance will prevent its rapid drying and the drying must be carried out below its melting point. The thickness of the layers is also of importance as some substances tend to form impervious layers on the surface during drying while other substances fall to powder and may be dried in large lumps.

*Humidity of the Air.* — The amount of moisture initially present in the air and the amount present in the air as discharged must be ascertained. This is a function of the temperature, and the per cent of humidity. This is the ratio of the amount of moisture in the air to the amount which would be present if the air were saturated at that temperature. This value gives no idea at all of the absolute amount of water in the air which

increases with the temperature for a given per cent humidity. For dryer calculations the amount of moisture must be known in terms of pounds or other specific units. This must also be given for a definite quantity of air. If the air is measured in cubic feet or other unit of *volume*, the temperature, pressure, and humidity must be given as the volume would vary with each of these conditions. A perfectly definite unit would be pounds of dry air.

Grosvenor [5] has calculated the following values on the basis of pounds of dry air:

Humidity = pounds of water vapor per pound of dry air.
Humid Heat = B.t.u. required to raise one pound of air plus its water vapor one degree Fahrenheit.

The *humidity* may be calculated from the vapor tension of water. At a given temperature, as for instance 122° F., the vapor tension of water is 92 mm. This pressure will be exerted in a vacuum or in saturated air. If the atmospheric pressure is 760 mm. the partial pressure of the air will be (760–92) 668 mm. The ratio by volume of air and water will be 668 to 92. The ratio by weight will be the product of the ratio by volume times the molecular weights which is 29 and 18 giving (29 × 668) 19,372 and (18 × 92) 1656. In terms of pounds of water per pound of dry air the value will be .0855. If the air is 75 per cent saturated the value will be .0641.

| °F. | Humidity | Humid Heat | °F. | Humidity | Humid Heat |
|---|---|---|---|---|---|
| 32 | .00376 | .239 | 100 | .0421 | .257 |
| 40 | .005046 | .24 | 120 | .0804 | .275 |
| 50 | .00757 | .24 | 140 | .1515 | .31 |
| 60 | .01094 | .2425 | 160 | .2955 | .378 |
| 70 | .0156 | .245 | 180 | .6494 | .546 |
| 80 | .0220 | .248 | 200 | 2.268 | 1.315 |
| 90 | .0307 | .252 | 210 | 15.817 | 15.9148 |

*Per Cent Humidity.* — The figures given under "humidity" represent the total amount of water vapor which one pound of air can take up at the temperature given. Under natural conditions, the air is seldom saturated. A determination of the per cent of

[5] Transactions of American Institute of Chemical Engineers, Volume I, page 184.

saturation would enable one to calculate from the table the actual amount of water vapor in the air. On heating the air to a given temperature, its capacity for carrying water would be increased. For instance, if air at 40° F. and 50 per cent humidity were being used, one pound of the air would contain (.005046 × .50) .002526 pound of water. On heating this air to 160° F. its capacity to hold moisture would increase to .2955 pound of water. It would therefore be able to absorb (.2955–.002526) .2930 pound of water at 160° F.

*Humidity of Exit Air.* — When the warm air comes into contact with the moist material to be dried and the water evaporates, heat is absorbed from the warm air which is cooled and therefore does not absorb the amount of water calculated. If contact between the air and material to be dried is sufficiently prolonged, equilibrium will be established and the air will be saturated at a temperature below that to which it was heated, namely: the wet bulb temperature of the air. If the air is reheated and contact with the moist material continued, an increased amount of water will be taken up by the air. The exact amount taken up may be calculated from the temperature and humidity of the exit air. The amount of heat which must be supplied may be calculated from the "humid heat" and the heat of evaporation of water.

*Volume of Air.* — When the number of pounds of air necessary to dry the required amount of material has been calculated, the volume of air in cubic feet may be calculated. This is necessary because the capacity of blowers is given in cubic feet per revolution or per unit of time.

*Maximum Amount of Air.* — As the air as used in driers varies considerably in temperature and humidity, the maximum amount of air must be provided for when designing driers. The condition of the air as to saturation on leaving the drier will depend upon the contact between the air and the moist material and also on whether the air is reheated after taking up the initial amount of moisture. If sufficient heat is supplied, the air will pass out of the drier saturated at as high or higher temperature than that at which it entered the drier.

The humidity of the air as well as economy in operation so far as heat is concerned will also depend very largely on the method of operation as to whether *parallel flow* or *counter current flow* is employed.

In *parallel flow*, the wet material is introduced at the same point as the hot dry air enters. The temperature to which many materials may be exposed must not exceed a definite limit. The moist material can be exposed with safety to a much higher air current than the dry material because when water is evaporating freely the temperature of the material does not rise much above the wet bulb temperature. On account of the large temperature difference at the hot end of the drier, evaporation is very rapid. As the material and the air pass through the drier, the temperature becomes lower so that the material is not exposed to excessive temperature. If such a material be passed through a drier counter current flow, it would be necessary to reduce the temperature of the hot air to avoid overheating the product. The efficiency of the drier would then be very much reduced.

Parallel flow is also advantageous when, as is often the case, a definite amount of moisture must be left in the product.

In the *counter current flow* method, the moist material is introduced at the point at which the air leaves the drier while the dried material leaves the drier at the point where the dry air enters. By this method the air will leave the drier fully saturated as it is in contact with moist material on leaving the drier. If the temperature of the air has been maintained by heating coils, the air will leave the drier carrying the maximum amount of moisture. This will result in economy of air and also of heat in operating the drier. As the hot dry air on entering the drier meets material which has passed through the drier and is therefore partially or nearly dried, very complete drying of the material will result. This method is therefore advantageous when complete drying of the material is desirable and when overheating or quick drying of the material is not to be feared.

*Intermittent Drier.* — Driers may also be constructed and operated as intermittent or continuous. The intermittent drier consists essentially of a compartment or room through which heated air is passed and into which the material to be dried is placed and allowed to remain until dried. The material may be held in trays or racks or suspended, depending on its character. This method lends itself admirably to material which must be dried slowly.

A wide range of temperature may be used in the compartment drier. Low temperatures are obtained by heating with steam or hot water. High temperatures are obtained by heating with

hot oil or the introduction of the combustion gases into the drier or by flues heated by combustion gases. At such high temperatures the drying is very rapid.

Movement of the hot air is obtained in a variety of ways. The heating coils may be so placed that the hot air rises in the drier and then descends as it cools due to the drying effect. A vent is provided at the floor for the escape of the cold moist gas, the fresh air being admitted to the heating coils.

In many driers air circulation is maintained by means of blowers or fans. Considerable variation is shown in the method of introducing the hot air and exhausting the cold moist air. In some cases the hot air is introduced at the floor and exhausted at the ceiling. In other cases the reverse method is employed. In other driers a transverse current is produced.

These methods will show a difference in thermal efficiency and also in uniformity of the product.

The amount of steam required for driers is generally 2 to 2.5 pounds of steam per pound of water evaporated.

*Continuous Drier.* — Continuous driers are constructed in such a manner that the material to be dried is moved by various mechanical means through the drier, the material entering moist and leaving the drier in a dry condition. This method gives a very uniform product. A continuous drier cannot be used unless the material dries in a relatively short period of time. Usually 5 to 6 hours is the limit of drying time for successful operation in continuous driers. The compartment drier is more advantageous when the material must remain in the drier for a longer time. Some materials may be left in the drier over night, the drier being discharged in the morning and recharged with fresh material during the day.

Where a process is continuous, it is always advantageous to use a continuous drier if this is feasible for other reasons. A more uniform product is generally obtained with a continuous drier. Both types of driers may be operated with vacuum or at atmospheric pressure.

*Tunnel Driers.* — Tunnel driers are constructed of considerable length with reference to width and are equipped with means of moving the material to be dried through the drier. Frequently this consists of light cars or trucks which run on steel rails. The material is spread on trays which are placed in racks on the cars. Suitable air spaces are provided for between the

trays to provide for air circulation. Cars loaded with moist material are pushed into one end of the tunnel which is filled with similar cars so that a car is pushed out of the tunnel by each car which is pushed in. In a similar manner material suspended from hooks free to move on a track or steel bar may be moved through the tunnel. The current of drying air is forced by fans through the tunnel which may contain heating coils at intervals. Driers of this kind are very efficient, require very little labor, and give a uniformly dried product. The details of construction must be designed to suit the particular kind of material to be dried.

The velocity of the air in tunnel driers is from 300 to 1000 ft. per minute. The velocity is greatest at the hot end and decreases as the air drops in temperature. If too low velocities are used the temperature in the tunnel will not be uniform on account of convection currents.

*Drum Drier.* — Drum Driers are well adapted for drying material which is produced in the form of a concentrated solution or paste. This drier consists of a drum which is heated to a suitable temperature by steam or other convenient source of heat. The drum which is mounted on a horizontal axis is rotated when in operation and the paste to be dried is fed onto the drum in a thin sheet which dries in less than one revolution of the drum and is scraped off by a shelf or knife edge in contact with the drum. By enclosing the drum, the drying may be carried out in vacuum. With material adopted to this type of drier excellent results are obtained.

Instead of a drum, horizontal rotating disks or plates may be employed. The material to be dried is fed on the disk in a thin sheet which is removed by a scraper and carried away by a suitable conveyor.

**Rotary Driers.** — A very efficient type of drier consists of a cylinder which is mounted on a horizontal axis provided with the mechanism for rotation (Fig. 93). This very commonly consists of a gear fastened to the outside of the shell. The gear engages a pinion keyed to a driving shaft. The shell is supported on rollers to facilitate rotation. Steel tires riveted to the shell rest on the rollers. The material to be dried is fed in at one end of the cylinder and is discharged at the other end. The movement of the material through the cylinder is facilitated by the slightly

inclined position of the cylinder and also by plates or shelves which are fastened to the inside shell of the cylinder. During the rotation of the cylinder, the material is continually picked up by the shelves and thrown through the hot air in the driers. The inclination of the shelves serves to move the charge forward.
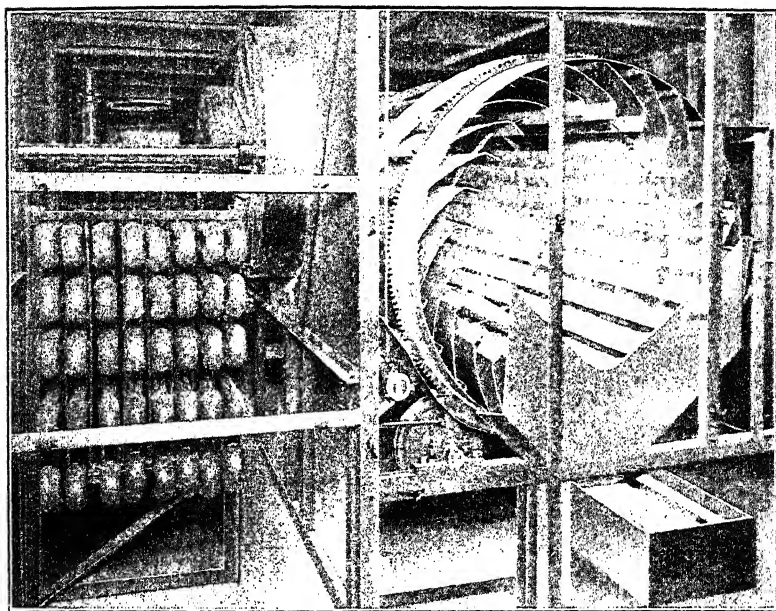


FIG. 93. Rotary Type Air Drier Showing Heating Coils, Fan, and Drum Containing Material being Dried.

*Methods of Heating.* — Rotary driers are heated in various ways depending upon the nature of the material to be dried and the temperature to which it must be subjected. If low temperatures must be maintained, a current of heated air may be employed. The cylinder may also be steam jacketed and steam pipes may be passed through the central portion of the cylinder. In this manner a high temperature may be maintained in the drier. The water evaporated must be carried away by means of a current of air. This may be produced by means of a blower or the drier may be connected with a stack by means of flues.

*High Temperature Driers.* — When high heat is required in the drier, the discharge end is connected directly with a furnace so

that the flue gases pass through the drier.   Suitable draft may
be produced either by a fan or by connection with a stack.    An
exhaust fan affords the best means of control and economizes
heat as draft through a stack can only be produced by means of
hot gases.   If it is undesirable to bring the flue gases into direct
contact with the material to be dried, the flue carrying these
gases may be passed through the center of the drier.   During
the rotation of the drier, the material will come into direct
contact with the hot flue which will also serve to heat the air
passing through the drier.

When very high temperatures are desired in the drier as when
the material must be calcined, the cylinder should be lined with
fire brick in order to act as a non conductor and also protect the
steel shell from the hot gases.   If the flue gases are passed through
the drier, a by-pass must be provided to avoid over heating in
case the drier stops.

*Thermal Efficiency.* — Driers of this type are very efficient and
economical of heat.   As the gases pass out of the drier in contact
with wet material, their heat and moisture carrying capacity are
fully utilized.   As the material leaves the drier in contact with
the hot dry gases, it is fully dried.   At this point some heat is
lost, as the material leaves the drier heated to the temperature
of the hot gases.   If it is not desirable to heat the material to such
a high temperature, the drier may be operated by parallel flow.
That is, the wet material may be introduced at the same point at
which the hot gases enter, and discharged at the other end of the
drier, where the now considerably cooled gases pass out.   By
regulating the amount of the hot flue gases entering the drier it is
possible to control conditions so that any desired amount of
moisture may be left in the material being dried.

**Spray Drying.** — This method of drying is applicable to con-
centrated solutions of a great variety of material both organic
and inorganic.   It is based on the principle that, if a liquid is
reduced to drops of sufficiently small size, the surface will be so
enormously increased that evaporation will be increased to such
an extent that the water in the droplets will be evaporated in
the time required to fall through a distance of a few feet.   The
method is particularly advantageous in the case of liquids which
form viscous solutions which are difficult to dry and also to
solutions of organic matter such as milk which is decomposed if

heated to even a moderately high temperature for even a short time. When such a liquid is atomized into dry air, evaporation is so rapid that the temperature instantly falls very considerably. The drying is therefore carried out at a low temperature and in a very short time. If material is being dried which forms viscous solutions but which can be heated to a high temperature, the drying is exceedingly rapid and therefore the method is advantageous. The dried product is always obtained in a finely divided condition rendering grinding or powdering unnecessary. This is an additional advantage.

In the operation of spray driers it is necessary to recover the fine material which is invariably held in suspension in the air currents. Some form of dust separator must be installed for this purpose. A very efficient type is the bag dust collector in which the dust laden air is passed through bags of suitable material.

*Drying Liquids.* — Spray drying is similar to evaporation in that it is a method of drying which is applied to a solution from which it is desired to recover a solid by evaporation of the solvent. It is applicable to liquids from which the solvent must be completely evaporated in order to recover the solid. It is generally most advantageous first to evaporate the solution in some form of evaporator designed for the concentration of the solution to the point at which the solid begins to separate or the solution begins to become thick and viscous.

*Spraying Device.* — The process involves the following steps: The liquid must first be atomized. It is desirable to produce a spray of small particles of uniform size. A suitable spraying device and chamber must be provided for this operation.

*Air Drying.* — The drying of the dispersed particles is accomplished by bringing them into contact with warm air. This operation must be carried out in such a manner that the moist particles are dried before they reach any part of the drying chamber. That is, only dry particles should impinge on the walls or floor of the drying chamber. In order to accomplish this, the particles must be so small that the moisture is completely evaporated in the very short time required for their fall. It is also necessary for the drying air rapidly to reach every part of the spray of wet particles. The heat necessary to evaporate the solvent is obtained from the air.

In the third place it is necessary to separate the fine particles of dried material from the air current used for drying.

*Vacuum Drying.* — Spray drying may also be carried out by introducing the spray of fine particles into a chamber in which a vacuum is maintained. In that case the solution to be dried must be heated, before it is sprayed, to such a temperature that sufficient heat is present to evaporate the solvent. This is not always possible.

*Jet Atomizer.* — Various types of atomizers have been developed and used. The first types developed were the jet atomizer in which the liquid under high pressure was forced through a small opening. Pressures of about 2000 lbs. per sq. inch have been found to produce particles sufficiently small for spray drying. Various difficulties have been met with in this type of atomizers. The minute orfice is gradually worn larger and may become clogged with impurities. The spray leaves the orifice in the form of a cone which spreads outward rendering it difficult to secure proper admixture of the drying air.
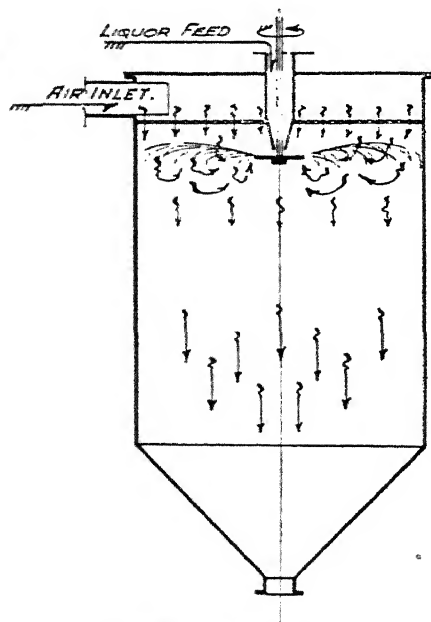
*Disc Atomizer.* — The disc type of atomizer consists of a rapidly revolving disk with angular projections at the perifery. The liquid to be atomized is fed to the center of the disc and projected from the perifery. Plain cup shaped discs have also been developed, the liquid being fed in some cases into the cup from above and in other cases the feed is directed into an inverted cup. In this type of atomizers there are no small apertures to clog and cleaning is relatively easy. The liquid also need not be delivered under high pressures. It is important that the liquid does not begin to dry at the perifery of the disc before it is atomized. This is prevented by directing a cold downward current of air in the immediate vicinity of the disc.



Fig. 94.  Spray Drier.

*Location of Air Inlet.* — A very important feature of the design of spray driers concerns the method adopted of securing satisfactory mixing of the drying air with the spray. If the atomizer is located in the lower part of the drying chamber and the air enters at the bottom with the outlet at the top of the chamber the dried particles will fall back through the incoming spray of moist particles. A similar effect will result if the atomizer is placed in the side of the drying chamber. The dried particles toward the upper part of the chamber will fall through the spray of moist particles.

*Mixing Air with Spray.* — If the atomizer is placed at the top of the drying chamber and the air current properly distributed
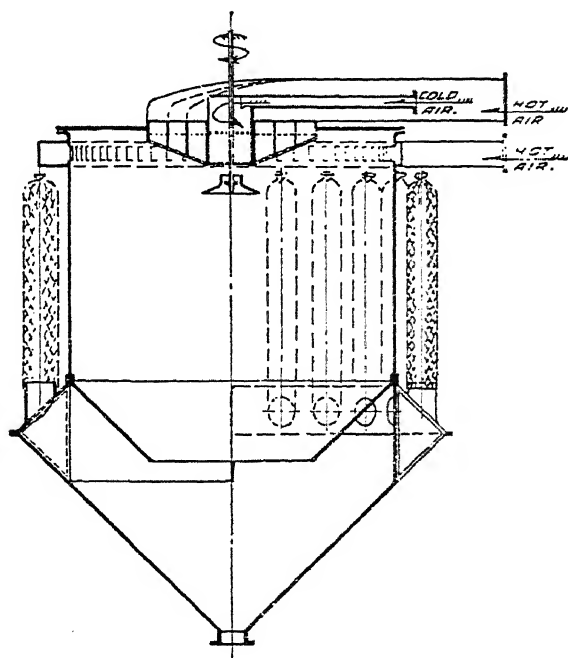


Fig. 95 Illustrates a Type of Spray Drier in Which a Current of Cold Air is Admitted Above the Disc Atomizer. This assists in atomizing the liquid by preventing it from drying before it is atomized and also cools the driving mechanism of the atomizer.

and directed downward, the moist particles will be dried as they fall to the bottom of the chamber. It has been found advan-

tageous to give the entering air a rotary motion corresponding to the motion of the spray. This facilitates mixing of the air with the spray. While some of the dried particles will fall to the bottom of the chamber, a considerable portion will be carried along by the air current. Means must be provided for the separation of this material from the air current. An excellent design consists of a double cone, the inner cone being truncated. As the air passes down through the inner cone, most of the powder is deposited and falls down to the outlet leading into the conveyer which carries the product away. The air passes up between the two coils to the air outlet. The velocity of the air is retarded by the large area for the air current. The remaining powder in the air is removed by means of bag filters.

*Heating the Air.* — The air used for drying may be heated by one of several methods depending upon the maximum temperature required. Heating by means of saturated steam is undoubtedly the best method when air temperatures not exceeding about 300° F. are used. This may be accomplished by means of steam at ordinary pressures not exceeding 120 lbs. per sq. in. the temperature of which is 340° F. The air to be heated is passed over the steam pipes, sufficient heating area being provided for the amount of air to be heated. As the heat transfer from the steam heated pipes to the air is proportional to the temperature difference the amount of heating surface required will decrease with increasing steam pressure and consequent increased temperature. It is not economical to use steam pressures higher than 120 lbs. on account of the cost of the equipment for high pressures. For temperatures up to about 550° F. hot oil may be circulated through the heating coils. This may be done at low pressures and high velocities giving high transfer so that relatively small heating surface is required. When higher temperatures are required, recourse must be had to electric heat or mercury vapor. If still higher temperatures are required, heating with direct fire must be resorted to.

*Amount of Air Required.* — The principles governing the amount of air required for removing a given amount of moisture have already been given. The warm, dry air on coming into contact with the spray of moist material will drop in temperature as it gives up its sensible heat which evaporates the water in the moist material. This process will stop when equilibrium is reached between the vapor tension of the moist material and that

| A. | DRYING CHAMBER |
|----|----------------|
| B. | AIR EXHAUSTS. |
| C. | PRODUCT OUTLET |
| D. | CONVEYOR |
| E. | CALCINER. |
| F. | HOT AIR FAN. |
| G. | ATOMISER |
| H. | MOTOR |
| I. | COLD AIR FAN. |
| J. | AIR DUCT. |
| K. | MANHOLE |
| L. | SIGHT GLASS |
| M. | FREE AIR INLET. |
| N. | HOT AIR FROM CALCINER |
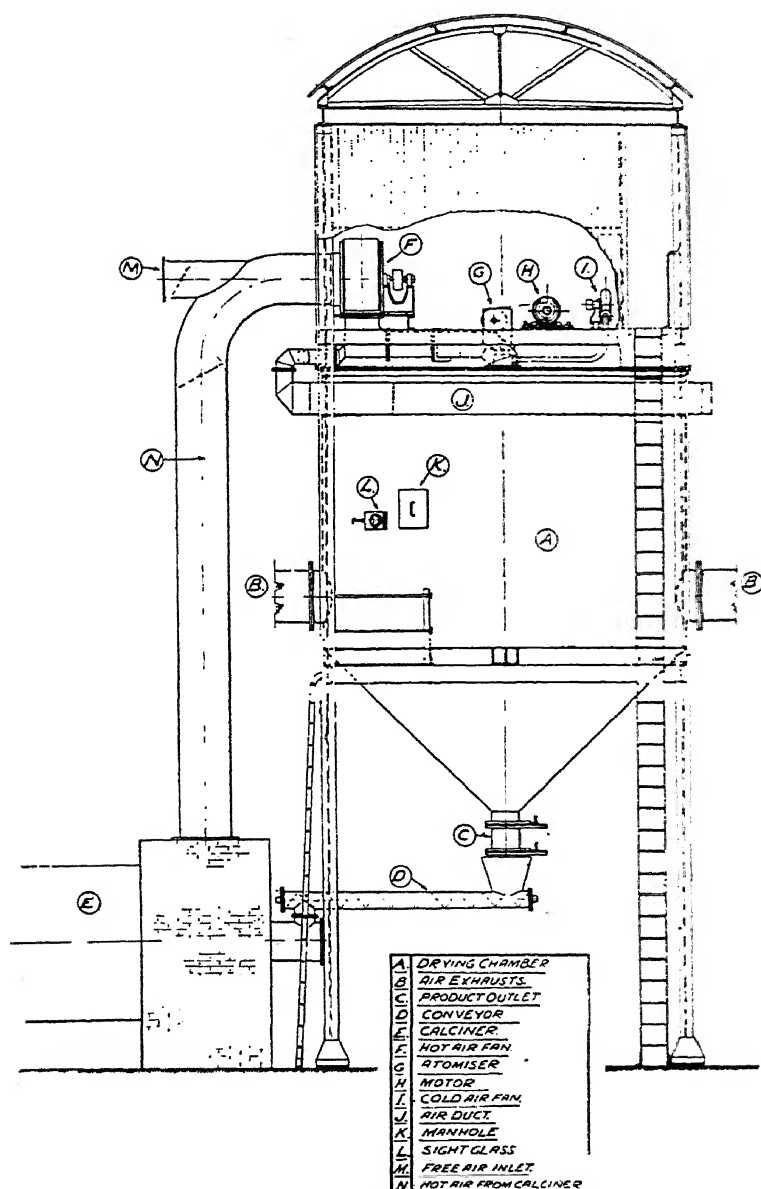
Fig. 96.   Illustration of a Complete Drying Unit Showing the Air Heating Unit, Drying Chamber, Air Exhausts, and Product Outlet.

of the air.   As in many cases the moist material consists of a water solution of the solid being dried, the vapor tension will be considerably less than that of pure water at the same temperature.   The drying capacity of the air will therefore be less than it would be for pure water.

*Thermal Efficiency*. — The efficiency of the process will increase as the temperature of the air used for drying is raised.   If air at 60° F. is heated to 265° F. and after passing through the drier is ejected at a temperature of 150° F., the amount of heat utilized is equivalent to the drop in temperature from 265 to 150° F. or 115°.   The remainder of the heat which had been added to the air represented by the difference between 60 and 150° or 90° is lost.   If radiation losses are negligible, the thermal efficiency will be 115/205 or 57 per cent.   If the air is heated to 500° and is rejected at the same temperature, that is, 150° F., the thermal efficiency will be much higher the maximum being 350/440 or 80 per cent.   As the air which is ejected in seldom saturated the thermal efficiency may be increased by recirculating and reheating part of the air and passing it through the drier again together with additional fresh air.

The employment of high temperature of the initial air not only gives a higher thermal efficiency but also gives a higher rate of evaporation on account of the higher heat transfer which gives an increased capacity of the plant.   The temperature of the air will be limited by injury to the material if overheated.

### Drier Problems

40. Calculate:

(a) Humidity of air in pounds of water per pound of dry air saturated with water vapor at 160° F.

(b) Saturated volume, that is, volume of one pound of dry air saturated with water vapor at 160° F.

41. A drier is to be designed to reduce the water content of 1000 pounds of material at 100° F. containing 50 per cent of water to the dry basis in one hour.   The entering air must have a temperature of 150° F. and .0156 lb. of water per lb. of dry air and leave the drier at 110° F. with 80 per cent humidity.   Calculate

(a) the amount of entering air in cubic feet per minute,

(b) B.t.u. per hour required to heat the air from 60° F.

(c) B.t.u. per hour to be supplied by heating surface within the drier.

(d) What will be the wet bulb temperature of the heated air entering the drier and the air leaving the drier?

42. The air supply of a drier has a dry bulb temperature of 65° F. and a wet bulb temperature of 55° F.   It is heated to 210° F. before entering the drier.   It leaves the drier 95 per cent saturated.   Assuming that no heat is lost from the drier by radiation:

(*a*) At what temperature will the air leave the drier?

(*b*) How much water will be evaporated by 100 cu. ft. of this air?

(*c*) If the air had been heated to 250° F. before entering the drier what would be your answer to (*a*) and (*b*)?

(*d*) Calculate the amount of heat required to raise the temperature of the air supply from the initial temperature of 65° F. to 210° F. Using the answer found for (*b*) how many B.t.u. of heat have been required to evaporate one pound of water?

(*e*) The air leaving the drier at the temperature found in (*a*) may be reheated to 210° F. and recirculated through the drier. Calculate the amount of water 100 cu. ft. this reheated air will evaporate, also the number of B.t.u. of heat per pound of water evaporated by this recirculated air.

# CHAPTER IX

## ELECTRIC HEATING

ROBERT M. KEENEY, E.Met.

**Selection of Heating Medium.** — The selection of the source of heat for a chemical or industrial process is an economic problem. The final choice should be dictated by the economics of the local situation, as shown by the overall cost of production. The mere fact that a heat unit in fuel oil may cost two and one-half times as much as a heat unit in coal, does not necessarily indicate that coal is the proper fuel. Gas may cost more per B.t.u. than oil or coal, but because of the possibility of its more efficient application may be by far the cheapest fuel. Electricity may cost more per heat unit than gas, oil or coal but because of higher furnace efficiency, ease of application, reduction of labor costs, and increased recovery due to close temperature control may prove the most economical source of heat to use.

Most of the applications of electric heating in the chemical industry are of two types: (1) processes in which electric heating must be used to obtain the temperature required for the reaction involved, and (2) processes which can be conducted with either fuel or electricity, but in which electric heating is used because it has resulted in the lowest overall cost of production.

**Development of Electric Heating.** — The application of electric heating to the chemical industry has developed along four broad lines during the past forty years: (1) arc furnace smelting of refractory ores and production of calcium carbide;

(2) High temperature resistance heating with an internal resistor imbedded in the charge or the charge acting as a solid resistor for production of chemical products such as carborundum;

(3) Low temperature resistance heating with the charge acting as a molten or liquid resistor as in the electrolytic aluminum furnace and in the electric steam generator; and

278

(4) Low temperature resistance heating by means of external metallic or non-metallic resistors as now employed in a wide variety of industrial applications.

From 1890 to 1900 electric heating was used mainly in the manufacture of clacium carbide, silicon carbide and artificial graphite, in the smelting of ores to produce ferro-alloys and in the electrolytic reduction of aluminum oxide to aluminum by Hall and Heroult, all of which are processes which can be conducted satisfactorily only in an electric furnace. These early developments were followed by electric furnace production of pig iron, cyanamide, alundum, and the melting of steel and brass. Early in the present century the fixation of nitrogen of the air by the electric arc became an established industry.

Low temperature resistance heating for industrial processes began about 1915 under the pressure of the war when it was first realized that the nickel-chromium alloys, discovered in 1904, were suitable for heating large industrial furnaces, as well as for heating small laboratory furnaces and use as thermocouples. Probably the construction of large electric heat treating furnaces heated by granular carbon resistors made apparent the tremendous field for electric heating in low temperature industrial processes with a suitable resistor available.

**The Arc Furnace.** — Large modern arc furnaces are usually designed for operation on three-phase alternating current, although for some processes conducted on a comparatively small scale the single phase furnace is often used. The arc furnace has developed with the electrical industry from the 100 kw. direct current carbide furnace of 1890 to the 15,000 kw. three-phase furnace of today. The early carbide furnace was located at the power plant with only a wall separating it from the low voltage direct current generator. The practice continued on the introduction of single-phase alternating current, the furnace being supplied directly from the generator. When two-phase and three-phase service became available, the energy was transmitted long distances at high voltages and transformed to the furnace voltage at the furnace, but at first, single-phase furnaces were still used and balanced in groups on the three-phase circuit. In a few years two-phase and three-phase furnaces came into use.

*Single-Phase Arc Furnace.* — Single-phase furnaces are of two types, one having a single carbon electrode connected in series

with a conducting hearth, commonly known as the Siemens type, and the other a furnace with two carbon electrodes connected in series, known as the "series" furnace.

The *Siemens type* of single-phase furnace is shown in Fig. 97, which illustrates a modern 150 kw. furnace used in the production of ferrotungsten. The furnace is of the "ingot" type, that is, ferrotungsten is not tapped, but builds up from the bottom into
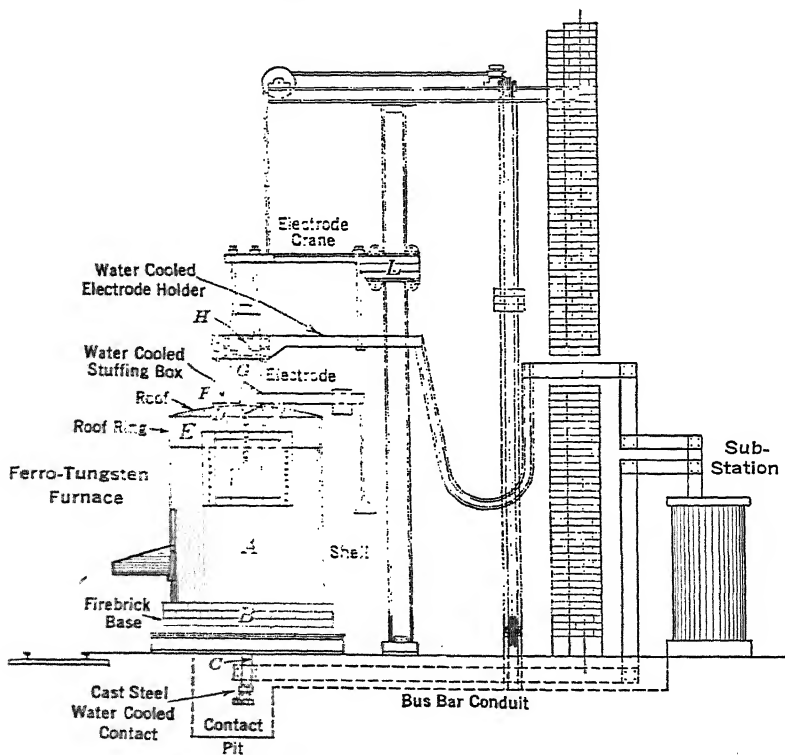


FIG. 97.   Siemens Type Single-phase Furnace.

an ingot or block weighing a ton or more, only the slag being tapped. The ingot principle was used in the first carbide furnaces which were simply unlined steel shells, a movable carbon bottom on a truck, and a single vertical electrode if the furnace was of the Siemens type but two electrodes if of the series type. The

early furnaces were inefficient both in energy consumption and raw materials. Their use prevailed in Europe until about 1905, when the size was increased from a maximum of about 300 kw. for the "ingot" furnace to 750 to 1,200 kw., and the carbide tapped. The tapping furnaces were lined with magnesite on the sides and had a carbon bottom. Some were stationary and some mounted on trucks. The power consumption and waste of material was much reduced by the larger tapping furnace.

The furnace shown in Fig. 97 has a steel shell, $A$, 5 ft. high and 4 ft. 6 in. diameter, the shell having no bottom. It rests on a fire brick base, $B$, into which is set a cast steel water cooled contact, $C$, forming the bottom electrode. A roof of fire brick, $D$, held in a steel roof ring, $E$, encloses the top. In the center of the roof there is a water cooled bronze stuffing box, $F$, through which the amorphous carbon or graphite electrode, $G$, passes. The electrode is supported in a bronze or steel water cooled holder, $H$, which is in turn supported by the motor driven electrode crane, $I$. Graphite electrodes of 5 in. diameter or amorphous carbon electrodes of 10 in. diameter are used. The furnace is operated at 50 to 75 volts from a single-phase furnace transformer equipped with primary taps for voltage variation. The primary of the transformer is connected across a three-phase, high tension, 60 cycle circuit. The electrode is regulated automatically.

*Tapping Carbide Furnace.* — A 750 kw. tapping carbide furnace operated in Norway is shown in Fig. 98. The furnace is of rectangular cross section having a shell 10 ft. long, 6 ft. wide and 5 ft. 6 in. deep. The side walls, $A$, are lined with 9 inches of rammed magnesite and the bottom $B$, is a rammed carbon block. The upper electrode, $C$, consists of four amorphous carbon blocks, 10 in. by 12 in. by 6 ft. long, set side by side to make an electrode 10 in. by 48 in. in cross section, which is suspended from the truss of the building in an electrode holder. Carbide is tapped at $D$. The furnaces are operated "open top," that is, with no roof or with a partial roof. In this particular plant some furnaces are directly connected to 65 volt alternating current generators.

There has recently been built in France [1] a single phase tapping carbide furnace of the conducting hearth type having a capacity of 5000 kw., which is considerably larger than any previously

[1] M. Arrouet. The Miguet Electrode and the Miguet Furnace, Trans. American Electrochem. Soc., 52, 335 (1927).

operated.    In the past the reactance of the furnace circuit has made difficult the construction of single-phase furnaces of such large size, but in this case it seems to have been made possible by unusually careful interlacing of the furnace busbars and cables.
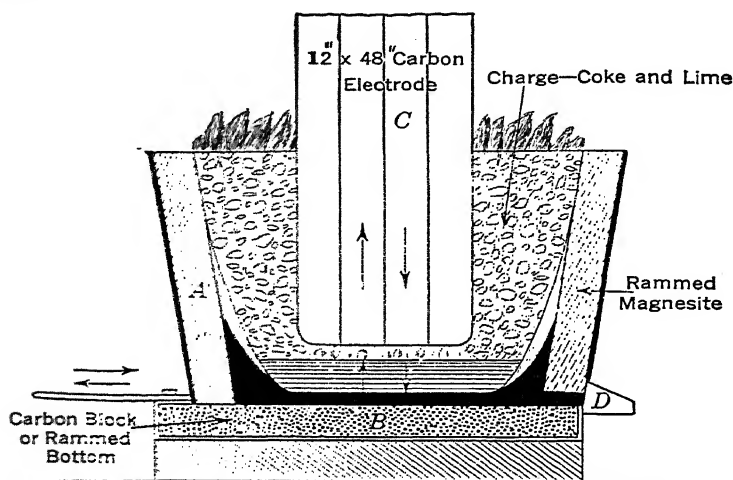


Fɪɢ. 98.   750 Kw. Single-Phase Tapping Carbide Furnace of Norwegian Type.

*Series Furnace.* — With the difficulties of design and operation of large conducting hearth furnaces, the "series" furnace, Fig. 99,
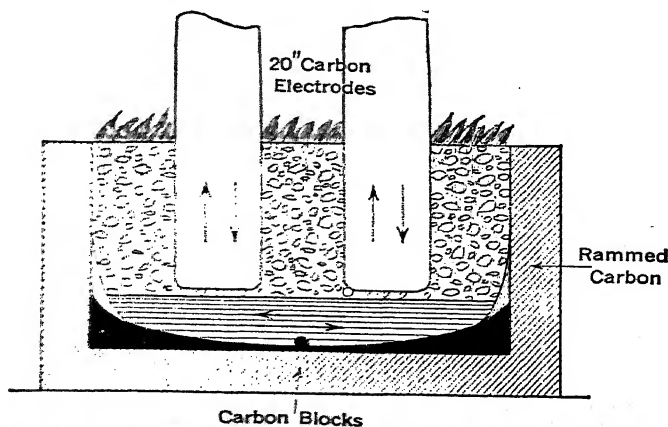


Fɪɢ. 99.   750 Kw. Single-Phase "Series" Type Carbide Furnace.

came into use. This furnace has two electrodes connected in series operating on a 60 to 70 volt circuit. Furnaces of this type are operated in the United States and Europe for production of calcium carbide, ferro-silicon, ferrochromium and high silicon synthetic pig iron. Continuity of production and a high load factor have been usually more easily attained in large single-phase furnaces of this type than in large conducting hearth furnaces.

*Three-Phase Arc Furnace for Manufacture of Calcium Carbide.* — The modern three-phase arc furnace is similar in general appearance to the "series" furnace but has three electrodes. Figure 100 illustrates an 1800 kw. open top furnace operated at 75
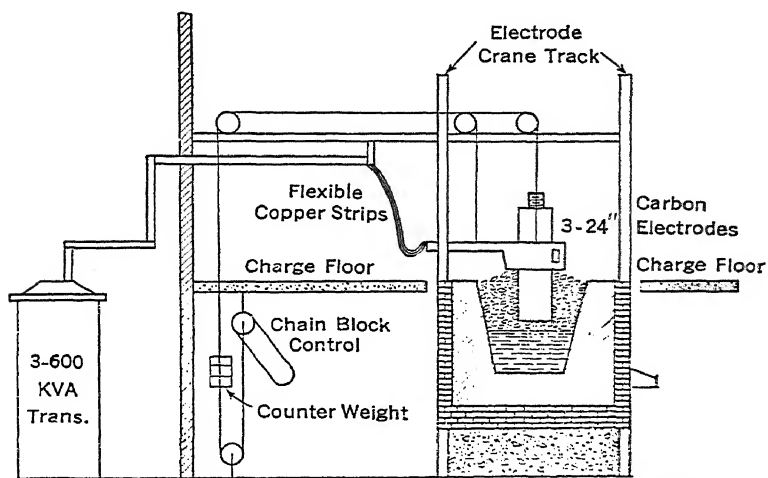


FIG. 100.   1800 Kw. Three-Phase Ferromanganese Furnace.

volts on production of ferro-alloys. The steel shell is of rectangular cross section, 18 ft. long, 9 ft. wide and 7 ft. deep, made of one-half inch plate, riveted and stiffened with channel iron and resting upon four concrete piers. The three 24 inch diameter amorphous carbon electrodes threaded for continuous feeding, are suspended on chains from a steel superstructure over which runs a hand crane with an electric hoist for installing electrodes. The shell is lined with a layer of common brick inside of which a refractory lining of dead burned magnesite, with hot pitch as a binder, is rammed. Raw material bins discharge onto a charge floor level with the top of the furnace. Metal and slag are tapped into movable pots through the same tap hole.

*Electrode Holders.* — Water cooled electrode holders are of the hinge type consisting of two halves, cast of 90 per cent copper bronze or of steel, the arms projecting to the back of the furnace being cast as a part of each half. The flexible connection to the holder arms is made by bundles of strip copper. There are no bolts or levers over the furnace top, the holder being clamped around the 24-inch electrode by three simple pins. The electrodes in this case are raised and lowered by chain blocks located beneath the charge floor. Very little regulation of electrodes is necessary in a smelting furnace of this size.

Furnaces of this general type of both rectangular and circular cross section are used for production of calcium carbide and ferro-alloys such as ferromanganese, ferrosilicon and ferrochromium. The furnace may have four or six electrodes and the type of holder and its suspensions varies, but the essential principle of electrodes in series and a non-conducting hearth prevails. As the size of the furnace increases the voltage must be increased to get the required capacity into the furnace, because of the increased reactance of the furnace with a higher amperage. A 10,000 kw. furnace may be operated at as high as 130 volts.

*Open Top Operation.* — These large arc furnaces are usually operated "open top" because it has been found that although the power consumption may be higher, the overall cost is lower, due to fewer interruptions of operation which may result from roof and lining failures and broken electrodes in a closed top furnace. With "open top" operation, the electrode holder stands the most severe usage of any part of the furnace, and improved design of holders during recent years has resulted in yearly load factors of 90 to 95 per cent. This is of very great importance to the operating cost of an electrochemical plant, because power is usually purchased for electrochemical processes on a flat rate per kilowatt year or per horse power year. Any failure of the furnace results in a higher operating cost per unit of product, because the plant must pay for energy not used.

*Electrodes.* — Next to the power and raw material costs, the most expensive single item in manufacture of calcium carbide and ferro-alloys is electrodes. The large three-phase furnace is usually operated with amorphous carbon electrodes, because their cost per unit of product is less in most situations and because they have greater mechanical strength. Small furnaces often have graphite electrodes for several reasons: they require a less

expensive supporting structure; they weigh less and are easier to handle; and they permit concentration of heating in a small space.

*Söderberg Electrodes*. — During the past five years, the use of the Söderberg [2] continuous feeding, self-baking electrode, has extended rather rapidly in Europe, but more slowly in the United States and Canada. It consists of a cylindrical shell of sheet steel, into which the electrode material of carbon, pitch and tar is rammed from a mixing floor above the top of the furnace. The steel shell and electrode are supported in a holder through which it can be slipped with current on the furnace. Sections of steel casing are welded on the top as electrode is consumed at the bottom. The newly added top is baked by conduction of heat up the electrode, and by the passage of the current through the electrode below the holder. A considerable part of the power load is carried by the steel shell. Electrodes of this type having a diameter as great as 39 inches are installed, and recently hollow electrodes have been developed.

*Electrode Regulators*. — The load of a large smelting furnace is so uniform that regulation of electrodes requires little attention and in many cases it is performed by hand. Some plants operate with electrode regulators of the Thury, General Electric and Westinghouse type, and others having them do not use them.

*Production of Calcium Carbide*. — Calcium carbide is produced in the arc furnace from a charge of lime and coke or anthracite coal according to the reaction:

$$CaO + 3C = CaC_2 + CO.$$
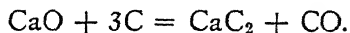
The procedure followed at the Muscle Shoals nitrate plant [3] during the short time it was operated at the end of the war, illustrates typical practice in the production of carbide. The charge was a mixture of 600 lb. of dry crushed coke and 1000 lb. of lime, which was shovelled from the charge floor into the furnace so as always to keep the furnace filled. After a furnace was in normal operation, it was tapped every 45 minutes by use of a tapping electrode and the hole plugged with powdered carbide. The power consumption was about 3300 K.W.H. per ton.

[2] M. Sem. Söderberg Electrode shows low operating cost, Chem. & Met. Eng., **32**, 865 (1925).

[3] C. H. Jones. Cyanamide Process Plant at Muscle Shoals, Chem. & Met. Eng., **23**, 182 (1920).

The plant contains 12 three-phase furnaces of 8325 kw. capacity operating at 130 volts. The furnace shell is 22 ft. long, 12 ft. wide by 6 ft. deep with a bottom of graphite electrodes and side walls of fire-bricks. The three electrodes are of the built-up type, an assembly of three carbon blocks each 16 in. square by 6 ft. 5 in. long, so that the finished electrode is 48 in. by 16 in. by 6 ft. 5 in. The water cooled electrode holder grips the electrode at the upper end. When the electrode becomes too short for use it is removed and a new one swung into position. Each electrode is covered with wire netting holding a protecting layer of asbestos cement to prevent air corrosion.

The flow-sheet of the plant is as follows:

```
                    Lime Trestle          Coke Trestle
                         |                     |
                    Limestone Silos        Coke Silos
                         |                     |
Coal Pulverizing Plant  7 Lime Kilns      4 Coke Dryers
                         |_____|
                                  |
                               Storage
                                  |
                            12 Lime Silos
                            12 Coke Silos
                                  |
                          12 Carbide Furnaces
                                  |
                          Carbide Cooling Shed
                                  |
                             Jaw Crushers
                                  |
                             Hardinge Mills
                                  |
                           Smidt Tube Mills
                                  |
                             Carbide Silos
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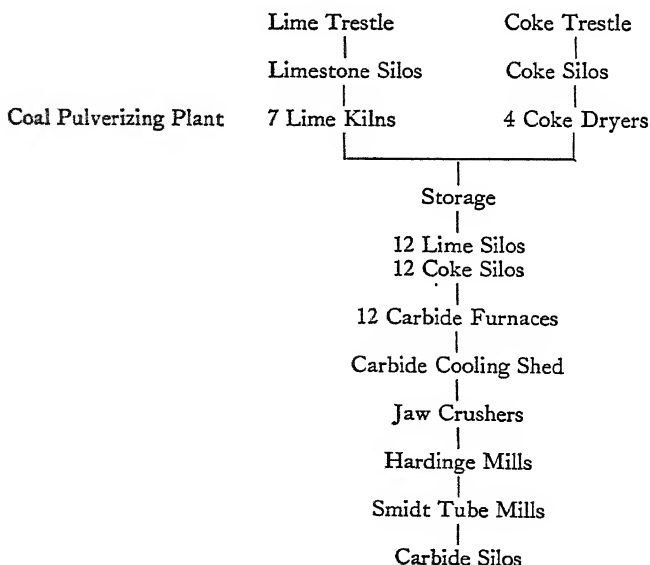
Arc furnaces producing calcium carbide have the following approximate power consumption and output per 24 hours:

| Size Furnace | K.W.H. per Ton Calcium Carbide | Tons—Calcium Carbide per 24 Hours |
|---|---|---|
| 150 kw., ingot | 6,500 | 0.4 |
| 300 kw., ingot | 5,000 | 0.8 |
| 750 kw., tapping | 4,500 | 3.3 |
| 1,200 kw., tapping | 4,000 | 6.0 |
| 1,800 kw., tapping | 3,800 | 10.0 |
| 5,000 kw., tapping | 3,600 | 30.0 |
| 8,325 kw., tapping | 3,300 | 55.0 |
| 10,000 kw., tapping | 3,200 | 70.0 |

*Three-Phase Arc Furnace for Manufacture of Phosphoric Acid.* — High grade phosphoric [4] acid is produced in the electric [5] arc furnace with simultaneous production of ferrophosphorus as a by-product. The greater part of the ferrophosphorus requirement of the United States is made in the blast furnace, but the electric furnace output is increasing. The raw materials are phosphate rock, coke breeze, quartz and steel scrap. For a 17 to 19 per cent phosphorus alloy, a three-phase open top furnace may be used, but for the 25 per cent product, the furnace has a closed top and the phosphorus vapors are oxidized with air and phosphoric acid also produced. The process of manufacture of phosphoric [6] acid as conducted in connection with production of ferrophosphorus, depends on the following reactions:

$$Ca_3(PO_4)_2 + 5C = 3CaO + 5CO + P_2,$$
$$CaO + SiO_2 = CaSiO_3,$$
$$P_2 + O_5 = P_2O_5,$$
$$P_2O_5 + 3H_2O = 2H_3PO_4.$$
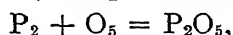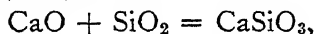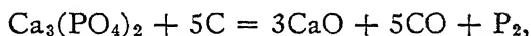
The phosphorus pentoxide fume is collected in a Cottrell precipitator and converted into phosphoric acid with water and steam. The product is superior to that produced by the sulfuric acid process from the standpoint of concentration and purity.

*Design of a Simple Arc Furnace.* — The single-phase, conducting hearth arc furnace is often used advantageously in the industrial plant for process experimental work and for small scale production because of its simplicity. Although past experience

[4] T. Swann. Production of Ferrophosphorus in the Electric Furnace, Min. & Met., 6, 4 (1925).

[5] B. G. Klugh. Some Considerations in Electrothermal Production of Phosphoric Acid, Chem. & Met. Eng., 35, 666 (Nov. 1929).

[6] W. H. Waggaman and H. W. Easterwood. The Future of the Pyrolytic Process for Phosphoric Acid, Chem. & Met. Eng., 30, 432 (1924).

is usually the best guide, the design of a small furnace is not complicated.   Assume that a 50 kw. furnace is required.   For most experimental work a voltage of 40 to 60 volts is suitable.   The line voltage available may be any of the following: 230, 460, 2300, or several intermediate voltages up to 13,800.   A transformer will be required.   Most of the operations will probably be at 50 volts, so that a single-phase furnace of 50 kw. capacity will use 1000 amperes at 100 per cent power factor.   The power factor, however, will be about 80 per cent, so the cables and transformer would have a load of 1250 amperes.   As a variable voltage transformer is desirable with the high voltage and full capacity tap 60 volts, a 75 KVA transformer is specified with primary windings suitable for the line voltage, and 60 volt secondary with taps in the primary to give secondary voltages of 60, 55, 50, 45 and 40 volts at a reduced kilowatt capacity. The transformer will carry a load of 1250 amperes at any of these voltages, so that on the 50 volt tap, 80 per cent power factor, the furnace will be using 50 kw.   With this information, the electrical manufacturer can supply the necessary transformer. To prevent violent fluctuation of the load, on small furnaces where the reactance of the furnace circuit is small, it is usually desirable to have a reactance coil in the primary or secondary circuit, giving 15 to 50 per cent reactance.   Other electrical equipment required will include: primary disconnecting switches, hand operated oil circuit breaker in the primary circuit with overload relay, a secondary voltmeter, an indicating wattmeter with necessary instrument transformers, and an integrating watthour meter to determine power consumption.

Consulting Table I it is found that either a 6-inch round or 6-inch square carbon electrode will carry a load $xf$ 1250 amperes. The round is preferable, because there will be no butts.

Possibly, however, facilities may not be available for handling electrodes weighing 102 lb. per 60-inch length, so it is desirable to use the lighter graphite electrode.   According to Table II, a graphite electrode of 2½-inch diameter will carry the load, but to get greater mechanical strength and greater length, it will probably be best to use the 3-inch diameter electrode forty inches long.   This electrode weighs only 16.6 lb.

*Construction of Furnace.* — A shell 36 inches in diameter by 30 inches deep, welded or riveted, of one-eighth-inch sheet steel, will be suitable for a 50 kw. furnace.   It should be lined to a

TABLE I — AMORPHOUS CARBON ELECTRODE DATA

*Round Electrodes*

| Diam. Inches | Area Sq. Inches | Weight per 60″ Length Threaded Lb. | Current Carrying Capacity Amperes | Current Density Amp./In.² |
|---|---|---|---|---|
| 6 | 28 | 102 | 1,200–1,700 | 40–60 |
| 8 | 50 | 166 | 2,000–3,000 | 40–60 |
| 10 | 79 | 253 | 3,000–4,800 | 40–60 |
| 12 | 113 | 359 | 4,500–6,800 | 40–60 |
| 14 | 154 | 484 | 5,400–8,500 | 35–55 |
| 16 | 201 | 670 | 7,000–11,000 | 35–55 |
| 17 | 227 | 692 | 7,900–12,500 | 35–55 |
| 20 | 314 | 957 | 11,000–17,300 | 35–55 |
| 24 | 452 | 1,350 | 15,000–25,000 | 35–55 |

*Square Electrodes*

| Diam. Inches | Area Sq. Inches | Weight per 60″ Length Unthreaded Lb. | Current Carrying Capacity Amperes | Current Density Amp./In.² |
|---|---|---|---|---|
| 6 | 36 | 116 | 1,500–2,200 | 40–60 |
| 8 | 64 | 219 | 2,500–3,800 | 40–60 |
| 10 | 100 | 338 | 4,000–6,000 | 40–60 |
| 12 | 144 | 487 | 5,500–8,500 | 40–60 |
| 14 | 196 | 653 | 6,800–10,800 | 35–55 |
| 16 | 256 | 891 | 9,000–14,000 | 35–55 |
| 20 | 400 | 1,355 | 14,000–20,000 | 35–55 |

National Carbon Co.

thickness of 12 inches on the bottom and 9 inches on the sides, giving a chamber of 18 inches diameter and 18 inches depth. The lining will depend on the work being done. If carbon is objectionable and the reaction to be performed is acid, a rammed mixture of ganister and linseed oil will be suitable. For a basic reaction, dead burned magnesite rammed in with pitch as a binder is preferable. With carbon, the bottom electrical connection may be made directly to the shell, but it has been found preferable to use a bottom water cooled steel contact passing up through the bottom of the shell and imbedded in the bottom for this purpose. This contact may be of the general shape of a round electrode, and based on a carrying capacity of 200–300 amperes per square inch of cross section.

TABLE II. — GRAPHITE ELECTRODE DATA

| Diam.<br>Inches | Length<br>Inches | Area<br>Sq. Inches | Weight<br>per<br>Piece<br>Lb. | Current<br>Carrying<br>Capacity<br>Amperes | Current<br>Density<br>Amp./In.² |
|---|---|---|---|---|---|
| 2 | 24 | 3.14 | 4.5 | 600–800 | 190–253 |
| 2 1/2 | 30 | 4.90 | 8.4 | 800–1,200 | 163–244 |
| 3 | 40 | 7.06 | 16.6 | 1,200–1,800 | 170–254 |
| 4 | 40 | 12.56 | 30 | 1,800–2,300 | 142–184 |
| 5 1/8 | 40 | 20.6 | 48 | 2,300–3,000 | 111–146 |
| 6 | 48 or 60 | 28 | 75 or 94 | 3,000–4,000 | 106–144 |
| 7 | 48 or 60 | 38 | 107 or 134 | 4,000–5,500 | 105–144 |
| 8 | 48 or 60 | 50 | 140 or 175 | 5,500–6,500 | 110–130 |
| 9 | 48 or 60 | 64 | 176 or 220 | 6,500–8,500 | 101–132 |
| 10 | 48 or 60 | 79 | 230 or 285 | 8,500–10,000 | 108–126 |
| 12 | 48 or 60 | 113 | 320 or 400 | 10,000–15,000 | 89–133 |
| 14 | 60 | 154 | 500 | 15,000–20,000 | 97–130 |
| 16 | 60 | 201 | 700 | 20,000–26,000 | 100–130 |
| 18 | 60 | 254 | 900 | 26,000–30,000 | 102–118 |

Acheson Graphite Company.

The electrode may be supported in the manner shown in Fig. 97 and controlled by a hand winch. For a small furnace, the electrode holder may be somewhat more simple, and water cooling is not absolutely necessary, but fewer operating difficulties will be experienced with the water cooled holder. The current density at the contact between the holder and the electrode should not exceed 50 amperes per square inch. Bolts for fastening the holder to the electrode should be avoided. No soldered connection should be used over the furnace, flexible copper strips or bare flexible cable with welded lugs being preferable.

If a roof is desirable, it should be about the diameter of the hearth above the bottom of the hearth, and will have a longer life if mounted in a roof ring (Fig. 97). A water cooled stuffing box in the roof is not necessary for a small operation. Firebrick makes a satisfactory roof. The use of insulating material between the lining and the shell is not recommended except in the case of a carbon lining, because it increases the efficiency of a small furnace very little and results in operating difficulties by slagging with the refractory when it becomes thin. The tap hole should have plenty of slope, and should be surrounded by fire brick next to the shell, the balance being formed by ramming

the furnace lining around a pipe when lining the furnace. It is sometimes desirable to have the furnace mounted for tilting to facilitate tapping. Shell diameters which have proven satisfactory for small single phase furnaces are: 100 kw., 4 ft.; 150 kw., 4½ to 5 ft.; and 250 kw., 6 ft.

*Power Supply for Arc Furnaces.* — Most central station systems supply three-phase power at a frequency of 60 cycles although a few systems are two-phase. In electrochemical centers the power supply is three-phase, but usually at a frequency of 25 cycles. The lower frequency is used because with it larger arc furnaces can be built owing to its characteristics resulting in a higher power factor for the load. The power company usually requires the user to maintain a power factor of 80 per cent at the time of maximum demand. On 60-cycle current it is difficult to maintain this in furnaces of much over 4000 kilowatt capacity, but with 25-cycle current a power factor of 80 per cent may be obtained in furnaces of 10,000 kilowatt capacity. Twenty-five cycle current, however, is not satisfactory for most central station customers because a large part of the load is lighting, and lights flicker on 25 cycle current. A three-phase power circuit is simply a combination of three single phase circuits carried in three conductors instead of two for the single-phase circuit, and is used because there is much less copper required to conduct the same current. A single-phase furnace is supplied from a three phase-circuit simply by connecting it to two sides of the three-phase circuit. Figure 101 shows three single-phase furnaces connected
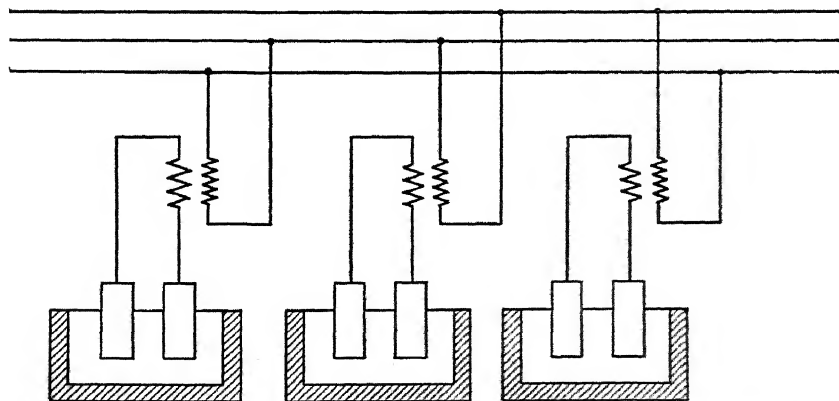


FIG. 101. Connection of Three Single-Phase Furnaces to Three-Phase Circuit.

to a three-phase circuit so that the load on each phase is balanced. Because of the unbalancing of the load, if only one single phase furnace is installed, most central stations will not supply a single-phase furnace of over 300 kw. capacity, unless the load is balanced, and many will not exceed 100 kw. The three-phase furnace is preferred by the central station, because it takes load on all three phases, as shown in Fig. 102. The single phase fur-
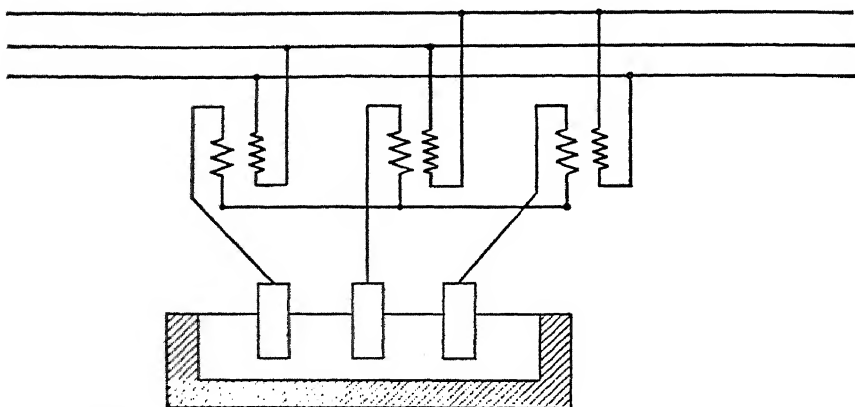


FIG. 102.   Connection of Three-Phase Furnace to Three-Phase Circuit.

nace is like a single phase motor, taking its power over two conductors, and the three-phase furnace is similar to a three-phase motor in that it is supplied by three conductors. Power factor and load factor have two entirely different meanings; power factor is lowered or raised by the electrical characteristics of the furnace, while load factor is affected by continuity of operation of the furnace.

**High Temperature Resistance Furnace with Internal Resistor.** — The high temperature resistance furnace with a resistor imbedded in the charge or the charge acting as a solid resistor, is used in the production of silicon carbide, artificial graphite and electrodes. The general design of the furnace has not changed since its first use, except for improvements in mechanical and electrical features. Internal resistance heating of a furnace of the shaft type is used in the manufacture of carbon bisulfide. The principle of the charge acting as the resistor, in this case a

liquid, is applied to electric generation of steam and to manufacture of chemically pure hydrochloric acid.

*Silicon Carbide Furnace.* — The Acheson silicon carbide furnace, Fig. 103, has a horizontal conducting core passing through the center of the charge.   As the furnace temperature increases,
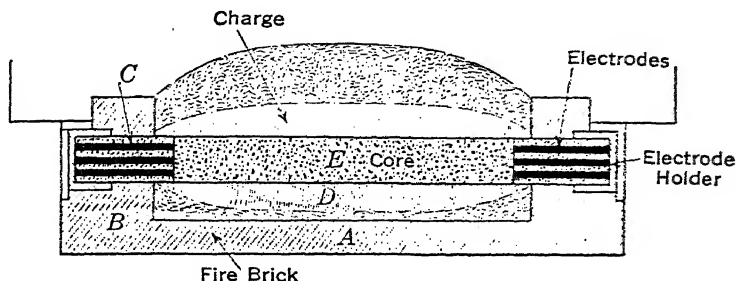


Fig. 103.   Acheson Silicon Carbide Furnace.

the charge adjoining the core undoubtedly also acts as a conductor of electricity.   The charge does not melt.   Carbon has a negative temperature coefficient, that is, its electrical resistance decreases with increase of temperature, so that the voltage must be lowered to maintain the same power imput, which is accomplished with the step-induction [7] regulator.   The furnace is necessarily intermittent, so that its only permanent parts are the base and end walls supporting the carbon electrodes and bronze electrode holders.   The side walls are simply temporarily laid bricks or removable iron forms.

The manufacture of silicon carbide is conducted in single-phase furnaces, up to 2000 kw. capacity having a length of 30 to 40 ft., width 6 to 10 ft. and height 6 to 10 ft.   In building the furnace the brick side walls or forms, *A*, are erected between the end walls, *B*, carrying the electrodes, *C*.   The furnace is then filled with charge, *D*, to the lower level of the core, *E*.   The core of screened coke, 1/4 in. to 1/2 in., is built up by hand to a circular cross section, 2 ft. to 3 ft. in diameter.   Contact between the core and the carbon electrodes at the end is made by a packing of fine carbon powder.   The remainder of the charge is added, covering the core.   The larger furnaces hold 70,000 lb. of charge. The hottest part of the furnaces reaches a temperature of 2220°

[7] E. E. Lehr.   The Step Induction Regulator, The Electric Journal, **17**, 510 (1920).

C. (4028° F.) which is the dissociation temperature of silicon carbide. Silicon carbide forms at 1840° C. (3344° F.). A 1500 kw. furnace is started with a load of 6000 amperes at 230 volts, but at the end of the 36 hours of heating will be using 20,000 amperes at 75 volts. The furnace cools for 36 to 48 hours, a complete cycle of loading, heating, cooling and reloading taking 108 hours.

Silicon carbide is made by heating a mixture of coke, sand, sawdust, and salt in a resistance furnace of the type shown in Fig. 103. The formation of silicon carbide takes place according to the reaction:

$$SiO_2 + 3C = SiC + 2CO.$$
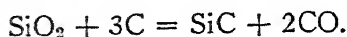
The sawdust makes the charge more porous so that the gases can escape and the salt assists in the volatilization of impurities as chlorides and in the operation of the furnace. A typical charge [8] is: coke 34 per cent, sand 54 per cent, sawdust 10 per cent and salt 2 per cent.

On the completion of a 36 hour run the furnace contains from the outside toward the center: (1) unconverted material, (2) fire sand and (3) high grade silicon carbide. The power consumption is 6000 K.W.H. per ton of silicon carbide. The flow sheet of a plant producing [9] silicon carbide is as shown in Fig. 104.

*Alundum.* — Another very important artificial abrasive, alundum, is not made in the resistance furnace but is the product of fusion of comparatively pure bauxite, which has been previously calcined, in a "series" arc furnace of the ingot type. A temperature of 2000° C. (3632° F.) is required to fuse bauxite. The power consumption is about 2000 K.W.H. per short ton. Alundum consists mainly of oxide of aluminum, $Al_2O_3$, with some iron oxide and silica present as impurities.

*Artificial Graphite Furnace.* — Artificial graphite is manufactured from anthracite coal in a resistance furnace similar to the furnace, except that the charge is covered with heat insulating material (Fig. 105). The production of artificial graphite from anthracite coal is a result of the formation of carbides of iron, silicon and aluminum from the ash of the coal and the later decomposition of these carbides at a still higher temperature, the metals being driven off as a vapor, leaving the carbon in the form

[8] A. Stansfield. The Electric Furnace, 292 (1914).
[9] Manufacturing an Artificial Abrasive, Chem. & Met. Eng., **31**, 501 (1924).

Coke
|
Storage
|
Crusher
|
Screen

Sand
|
Storage

Salt
|
Storage

Sawdust
|
Storage

Weighing

Mixers

Carbon Cores

Electric Furnaces          Electric Furnaces

Mill          Crushing Rolls

Acid Washer

Water Washer

Hydraulic Classifier          Rotary Dryers

Carborundum Flour          Magnetic Separator

Screens

Silicon Carbide Grains

Storage
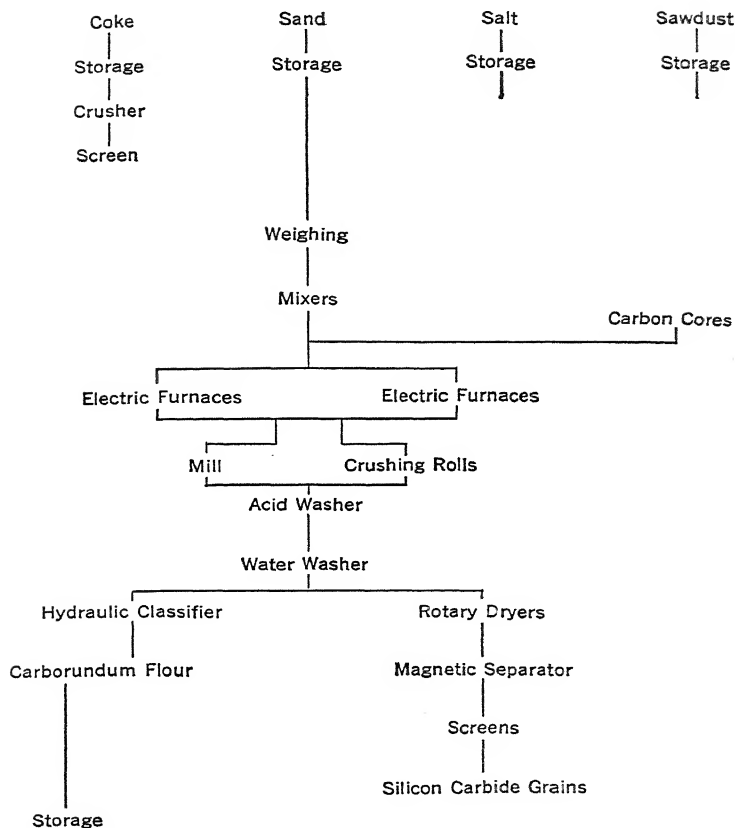
FIG. 104.   Flow Diagram of the Manufacture of Silicon Carbide.
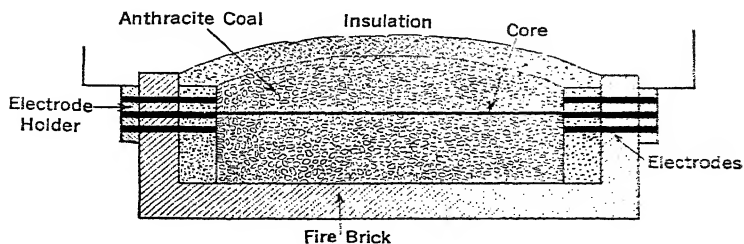


FIG. 105.   Acheson Graphite Furnace.

of graphite.    The furnace is heated for 20 to 24 hours and cools 4 to 5 days before being dismantled.    The power consumption is about 3000 K.W.H. per ton of graphite.

A similar type of furnace is used for graphitizing electrodes and for baking carbon electrodes except that in this case the charge of electrodes packed in petroleum coke acts as the resistor, there being no core.    The amorphous carbon electrodes to be graphitized are made of high ash anthracite coal and the same reaction takes place as in the production of artificial graphite. The furnace attains a temperature of 2000° C. (3632° F.), and the power consumption is 3 to 5 K.W.H. per lb. of electrode graphitized.    A graphite electrode furnace [10] cycle is operated approximately as follows: Loading, one to two days; on power, three to six days; cooling, 20 to 30 days; unloading one or two days, giving a minimum cycle of 25 days and a maximum of 40 days.

*Carbon Bisulfide Furnace.* — Carbon bisulfide is one of the few chemicals manufactured in the electric furnace.    It has been produced in the Taylor furnace for about twenty-five years according to the reaction:

$$C + S_2 = CS_2.$$
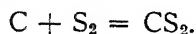
A recently built plant of five tons daily capacity has four furnaces [11] of the type shown in Fig. 106, which consists of a cast iron shell lined with refractory material, *A*, and is heated by the resistance of a bed of broken carbon, *B*, distributed over the entire cylindrical space between the water cooled electrodes, *C*. Charcoal is introduced periodically at the top of the furnace through the hopper, *D*.  Liquid sulfur is introduced from a melting kettle through a liquid seal and is delivered near the center of the hot zone, where it is vaporized instantly and reacts with the hot charcoal.    Carbon bisulfide, hydrogen sulfide and other sulfur compounds leave the furnace through the pipe, *E*, and enter the condenser, *F*, where the bisulfide, *G*, is recovered and the impurities are washed out continuously by means of overflow water.

The furnace operates at a maximum temperature of 1000° C. (1832° F.) on 440-volt two-phase current, through transformers

[10] 3. C. L. Mantell.   The Technology of the Carbon Electrode Industry, V, — Chem. & Met. Eng., 27, 312 (1922).

[11] G. A. Richter.   Manufacture of Carbon Bisulphide, Trans. Amer. Electrochem. Soc., 42, 253 (1922).

having variable voltage taps. The power consumption is 1000 to 1400 K.W.H. per short ton of washed carbon bisulfide recovered. There is a loss of 20 per cent of the sulfur charged.
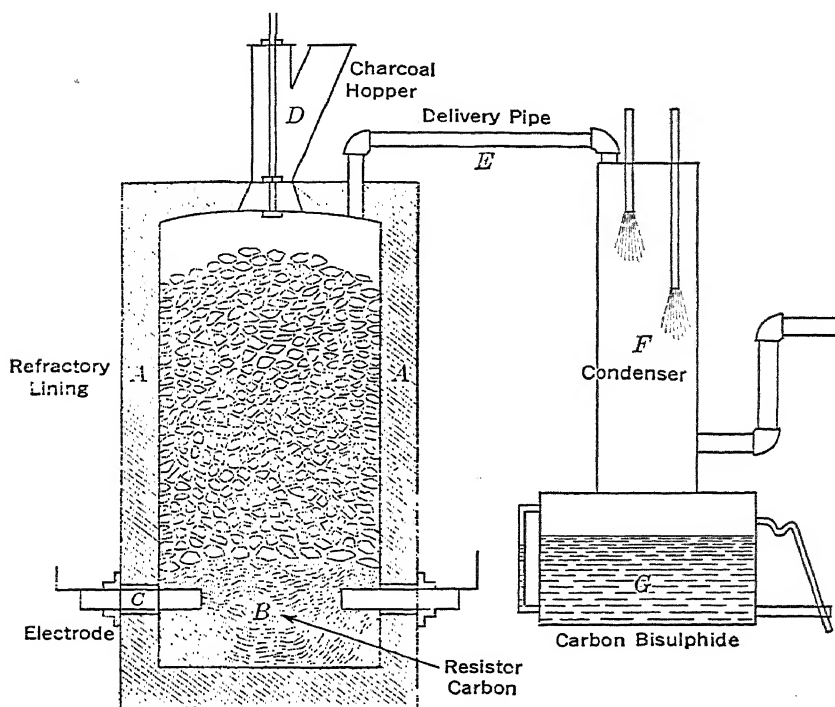


FIG. 106. Carbon Disulphide Furnace.

**Liquid Resistor Heating.** — *Steam Generator.* — At Arvida [12] and many other aluminum plants and pulp mills, steam is being generated in electric boilers. Electric steam generation is practical under these conditions because aluminum and pulp plants have usually been located at remote points where large hydro-electric developments are possible. Cheap power is essential. At remote points coal usually becomes expensive, so that steam may possibly be made more cheaply by electric generation.

It is understood that the cost of coal delivered at Arvida is $8.00 per short ton and electric power costs $8.00 per horse

[12] R. S. McBride. Cheap Power an Industrial Magnet, Chem. & Met. Eng., **33**, 724 (1926).

power year.   One kilowatt hour is equal to 3412 B.t.u.   For production of one pound of steam at 100 lb. per sq. in. pressure from 150° F. (67° C.) feed water, 1070 B.t.u. are required.   To produce 100 lb. of steam there will be used 31.3 K.W.H. at 100 per cent efficiency or 32.1 K.W.H. at the 97.5 per cent efficiency obtainable in the electric boiler.   At 95 per cent load factor, power at $8.00 per horse power year costs 0.13 cent per K.W.H. The fuel cost of making 100 lb. of steam in the electric boiler is $0.042.   The fuel boiler produces about 7.5 lb. of steam per lb. of coal, so that the production of 100 lb. of steam requires 13.3 lb. of coal.   With coal at $8.00 per ton, the fuel cost of 100 lb. of steam is $0.053 or 26 per cent higher than the cost of electrically generated steam.

The electric steam [13] generator consists essentially of a closed pressure vessle, to which is connected a source of water supply and from which water may be drawn off at the bottom and steam at the top.   Electric energy is made to flow through the water from an electrode in the form of a plate or tube to the shell of the vessel, or to the metallic inner lining.   Alternating current energy is used at a voltage varying from 110 to 22,000 volts. For three-phase operation there are three electrodes in one vessel, or three vessels with one electrode in each are used with the outer shells connected together in star.   There is no heating surface, the generation of the steam taking place throughout the water so that there is no part of the boiler above the temperature of the water.   The efficiency of the electric boiler is from 90 to 97.5 per cent, with a production of 2.8 to 3.1 lb. of steam per K.W.H.

The boiler, Fig. 107, consists of the tank $A$; the electrode $B$, supported from above; $C$, connection to other tanks of a three-phase installation; a grounded inner shell, $D$; a feed water opening, $F$; a funnel shaped casting, $E$, for deflection of the feed water around the sides of the tank; a bleeder, $G$; and a steam outlet, $H$. The boiler shown is one of three tanks of a 25,000 KVA, 6600 volt unit.

*Distillation of Chemically Pure Hydrochloric Acid.* — A new continuous process for the manufacture of chemically pure hydrochloric acid has been developed by the Grasselli [14] Chemical

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[13] P. S. Gregory.   Electric Steam Generators and Their Application, Trans. Amer. Electrochem. Soc., **42**, 215 (1922).

[14] C. M. Hoff.   The Development of the Process and Equipment for the Manufacture of Chemically Pure Acid by Electrical Distillation, Trans. Amer. Electrochem. Soc., **53**, 279 (1928).

Steam

*H*

*C*

Connection
between Tanks

*B*
Electrode

*D*

Grounded Inner
Shell

*A*
Tank

Deflector

*E*

Feed *F*

Bleeder *G*
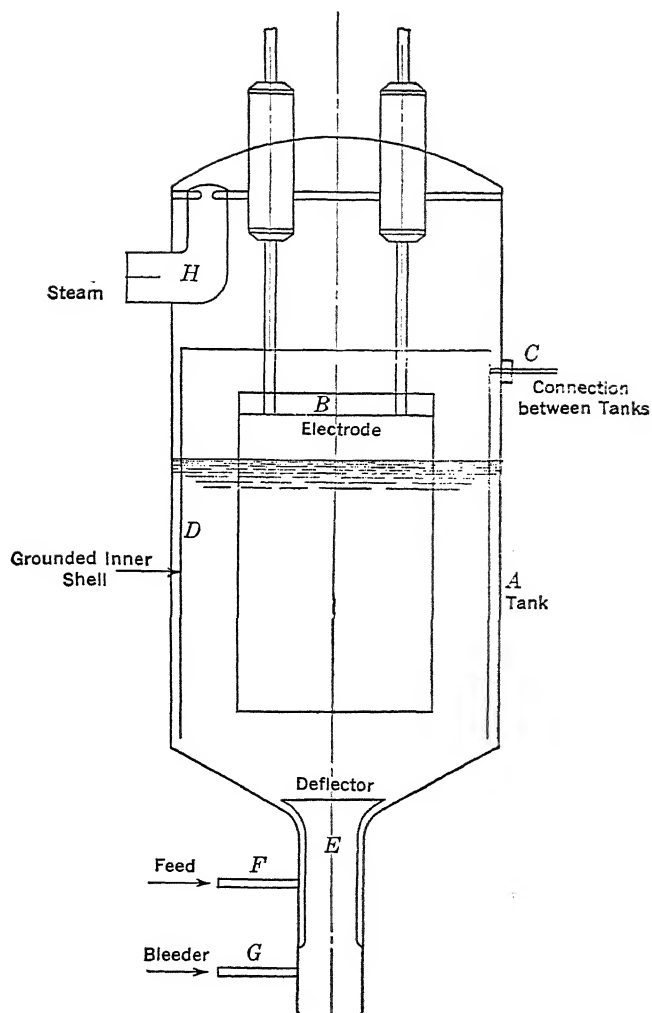
FIG. 107. One Tank of 25,000 Kw. Electric Steam Generator.

Co., using electric heating for distillation of commercial acid. The heating is from the resistance of the acid to passage of the current.   The equipment, Fig. 108, consists of a retort cut from a
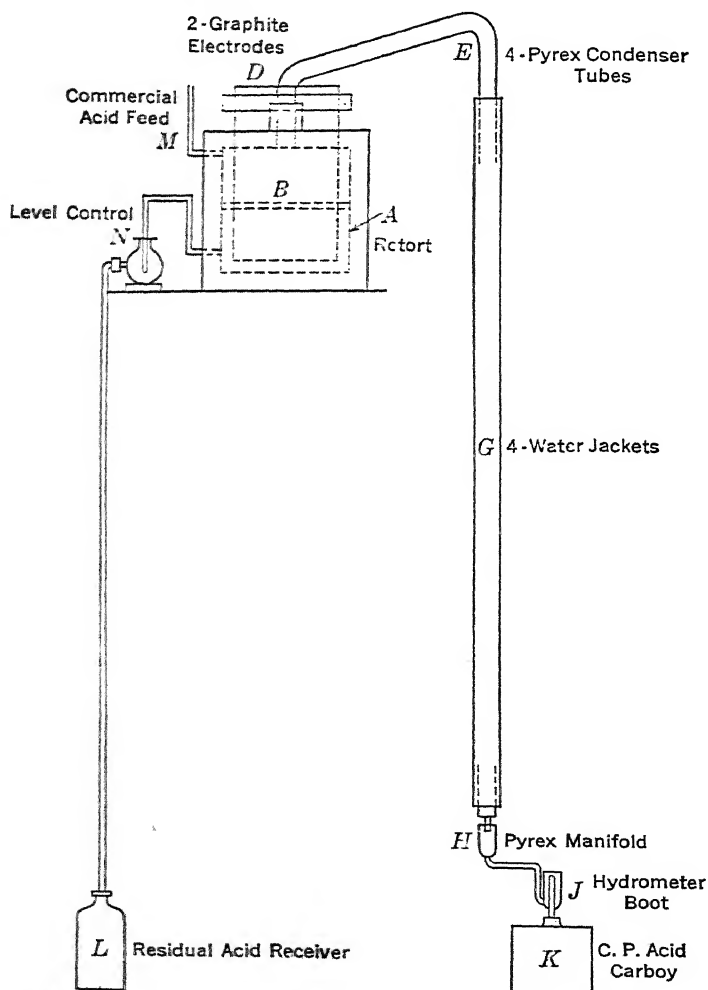


FIG. 108.   Apparatus for Production of Chemically Pure Acids.

block of granite, $A$; two graphite electrodes, $D$; four pyrex condenser tubes, $E$; four water jackets, $G$; a pyrex manifold, $H$;

hydrometer boot, $J$; and carboy for the C.P. acid, $K$. The commercial acid, 21.5 to 22.5° Bé., is admitted through $M$, and kept at the level, $B$, by means of a level control $N$. The residual acid receiver is at $L$. To prevent carrying over of iron salts, the end of the condenser tube adjoining the retort is filled with 6 or 8 inches of loosely packed glass wool. The retort is made in two parts, with the joint as far above the acid level as possible, and is sealed with Blue Cape asbestos. Phosphoric acid is used for luting connections to the retort manifold. In order to obtain a low current density and prevent electrolysis the electrodes are large, 6 in. wide, 1 in. thick by 30 in. long, and are drilled with small holes to allow circulation. The equipment has a capacity of 180 lb. of C.P. acid per hour. One part of the residual acid must be produced per seven parts of C.P. acid to prevent too high concentration of impurities in the retort.

One kilowatt hour makes as much C.P. acid as did 7.6 lb. of coal by the old process, so that the heating cost will probably be lower with electricity than with coal in most localities. There are a number of other advantages. The new equipment requires less than half the floor space, and has twice the capacity of the former apparatus. The room is at normal temperature and almost free from fume, contrasted with the very poor working conditions which formerly existed. One man now does the work of the seven men operating the old still. This process was developed for the commercial production of C.P. hydrochloric acid, but is also being used for the manufacture of C.P. nitric acid, and is readily adaptable to other processes requiring distillation.

**Resistance Heating by External Resistors.** — Within the past five years resistance heating by external metallic or non-metallic resistors has been applied gradually in the chemical industry for heating at comparatively low temperature 500° F. (260° C.) to 2500° F. (1371° C.). Types of heaters which have been used are the following:

1. The nickel-chromium clamp-on or strip heater, Fig. 109$A$, for heating tanks, piping and ovens to temperatures of 1000° F. (538° C.).

2. The immersion heater, Fig. 109$B$, for solution heating and steam generation up to 100 lb. pressure and another type, Fig.

109, for melting salts or metals up to temperatures of 750° F. (398° C.).

3. The nickel-chromium oven heater, Fig. 110, for temperatures up to 750° F. (399° C.).

4. The nickel-chromium furnace heating element, Figs. 111, 112 and 113, for temperatures up to 1850° F. (1010° C.).

5. The silicon carbide and carbon resistor for temperature up to 2500° F. (1371° C.).
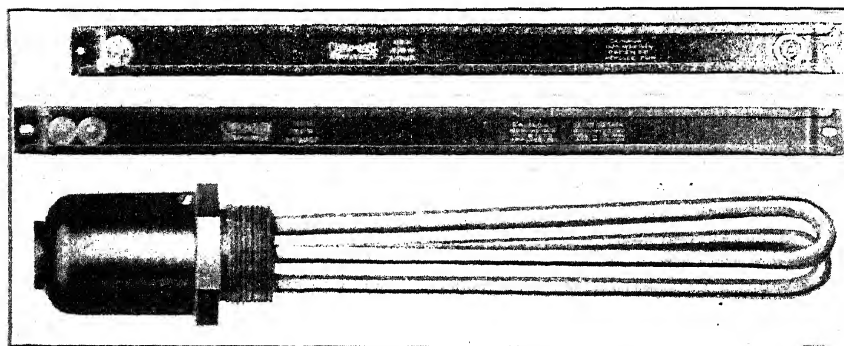


FIG. 109.   *A*—Clamp on or Strip Heater; *B*—Liquid Immersion Heater.

*Clamp-on or Strip Heater.* — In appearance the strip heater resembles a steel bar, and is usually 1 1/2 in. wide by 3/16 in. thick with a length of from one to 6 ft.   One form of strip heater consists of a flat nickel-chromium ribbon wound on mica and wrapped in mica, with the element thus insulated, assembled under pressure in a steel case, at each end of which there are terminals to which the ends of the ribbons are connected.   The most commonly used length is the 24 inch heater with 500 watts capacity for operation on 115 or 230 volt circuit.   The mica insulated strip heater is suitable for application where the heater temperature does not exceed 750° F. (399° C.), which means that it should not be applied for a process temperature exceeding 500° F. (260° C.).

Another strip heater, now having a wide use, is of the flat strip type, but has the nickel-chromium resistor imbedded in magnesia.   This heater may be used at a considerably higher temperature range than the others, 1000° F. (539° C.).

*Applications.* — There are two general applications for strip heaters: (1) air heating and (2) heating tanks, pipes or plates to

which the heater is clamped. Air heating applications are very numerous, particularly in the heating of isolated buildings thus eliminating long steam lines which are expensive to maintain and operate. Many strip heaters are used in low temperature baking and drying ovens. Strip heaters are in very successful operation for the drying of barrels.[15]

Next to air heating, the greatest application of strip heaters has been in the heating of pipes and tanks containing water, pitch, oil or chemicals. In one chemical plant having oils and fats, which congeal easily, flowing through pipes from one piece of equipment to another, electric heating has been an important factor in maintaining a high rate of production. Formerly, it was the custom for the operators to spend several hours each morning with blow torches warming pipes and valves, but with the application of strip heaters, backed by insulation, the plant is in operation a few minutes after the switches are closed.

Electric heating with strip heaters or other types of heaters can often be applied most economically in the chemical plant by combination with steam heating. In such cases the electricity provides the superheating beyond the temperature limits of steam. In one chemical plant operation [16] where 572° F. (300° C.) was required, a temperature of 445° F. (230° C.) was obtained with steam at 200 lb. pressure. The required 572° F. (300° C.) was secured by electric heaters clamped to the outside of the tanks. By this procedure only 75 kw. of electric heaters were necessary, whereas without the use of steam for the lower temperature, 400 kw. would have been needed.

*Immersion Heater.* — The immersion heater for solution heating, Fig. 110, consists of a nickel-chromium wire in the form of a helical coil which is insulated from the tubular casing of steel, copper or monel metal by powdered magnesia, the assembly of the coil in the tube being made under high pressure. The tube is brazed to a threaded head which can be screwed into a tank or pipe fitting. For solutions which do not attack it, this heater has a wide range of applications. Recently heaters have been made of a nature suitable for use in weak sulfuric acid solution. In applying the heater it should be understood that it must always

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[15] R. M. Keeney. Some Applications of Electric Heat in Chemical Industries, Chem. & Met. Eng., 32, 922 (1925).

[16] C. Field. Some Odd Applications of Steam, Chem. & Met. Eng., 34, 577 (1927).

be immersed in the liquid or it may fail.   The heater is suitable for pressures up to 100 lb. Calcium or alkali compounds which may deposit a crust on the heater may cause failure due to heat not being dissipated rapidly from the heater.   The heaters are of capacity up to 5 kw. for operation on 115 or 230 volt circuits.
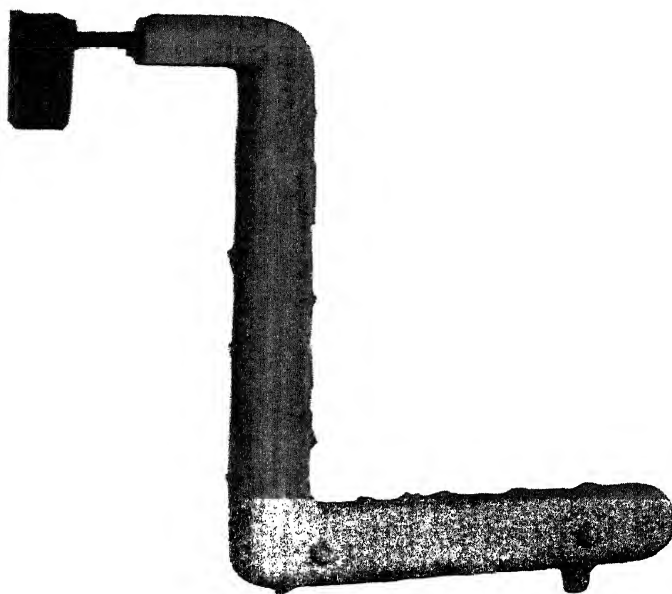


FIG. 110.   Molten Metal Immersion Heater.

Another type of immersion heater is the cast heater, Fig. 110, for heating salt baths and melting metals up to a temperature of 750° F. (399° C.).   The heating element is the same as the solution immersion heater but it has iron cast around it to give proper dissipation of heat.

*Oven Heater.* — The oven heater, Fig. 111, was designed to meet the requirements of the automobile industry for a heater to operate continuously at a maximum oven temperature of 550° F. (288° C.) but in small ovens, it has been operated at a temperature of 750° F. (399° C.), above which temperature it should not be used because of the tendency to warp out of shape to such an extent that the heater short circuits or grounds and fails.   The heater consists of a steel supporting frame with flanged steel

ends, fastened together by two steel rods in the same vertical plane, each of which carries a series of cylindrical fire clay spool insulators over which the nickel-chromium ribbon resistor is wound.
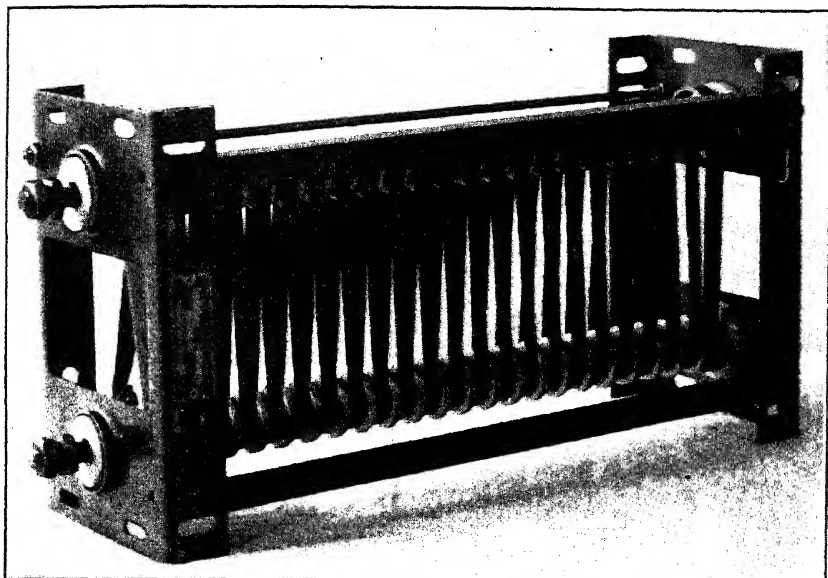


FIG. 111.  Nickel-Chromium Oven Heater.

*Metallic Furnace Heating Element.* — When power is comparatively low priced, as in isolated localities of Canada and Sweden, furnace coils have been recently applied to large pot furnaces for dehydrating caustic soda [17] and potash solutions of an initial concentration of about 50 per cent.  In a Swedish plant the power consumption is 0.45 K.W.H. per lb. of caustic soda, which resulted in a lower cost than with coal heating in that particular locality.

*Caustic Soda Pots.* — The Riordon [18] Pulp Corp., Temiskaming, Quebec, dehydrates caustic solution containing 60 per cent water in 500 kw. pots, equipped with furnace coils.  The pots are 10 ft. in diameter by 6 ft. deep.  A temperature of 1200°

[17] G. Angel.  Determining Heat Consumption for Caustic Dehydration, Chem. & Met. Eng., **34**, 683 (1927).

[18] Fusing Caustic Soda with Electric Heat, Fuels and Furnaces, 251 (Feb. 1928).

F. (649° C.) is reached in 6 hours, and held for 40 hours, after which the temperature is increased so that it is 1800° F. (982° C.) in 10 hours more when the caustic is solid. The total cycle is 56 hours. In this period 75,000 lb. of solution runs into the pot with an evaporation of 45,000 lb. of water. The pots produce 60 tons of caustic soda per week with a power consumption of 1350 K.W.H. per ton.
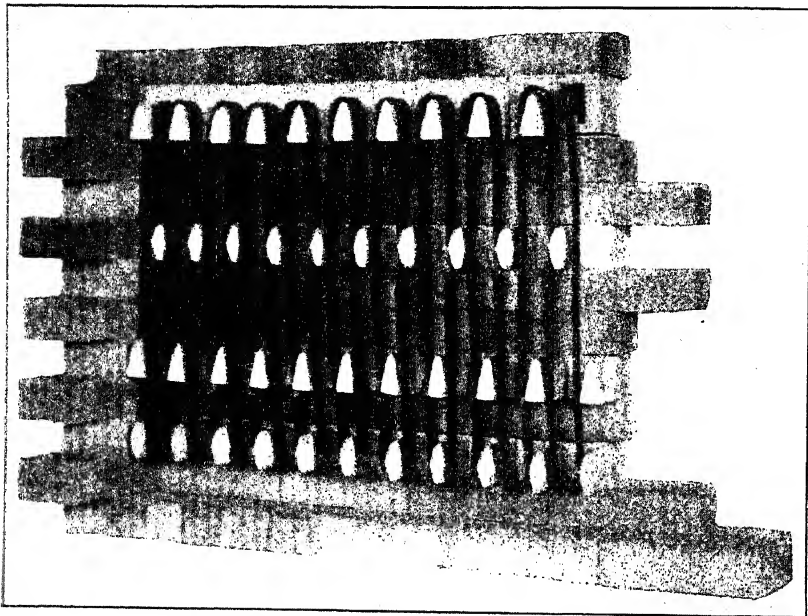


FIG. 112. Ribbon Type Furnace Resistor.

*Non-Metallic Furnace Heating Element.* — Before the use of the metallic resistor on a large scale, the granular carbon resistor was widely used for experimental work, and later applied to large industrial heat treating furnaces. With the development of the nickel-chromium resistors it passed out of use. Recently it has been applied successfully in a large continuous furnace for firing ceramic ware at a temperature beyond the limits of the metallic resistor. Another recent development is a resistor of silicon carbide moulded in the form of a pencil. This resistor is satisfactory for temperatures up to 2500° F. (1371° C.) and is now being applied with increasing frequency to furnaces for the

heat treatment of high speed steel at temperatures exceeding 2000° F. (1093° C.). While both of these elements open up a field of high temperature resistance heating, their use should be confined to temperatures exceeding the safe limits of the nickel
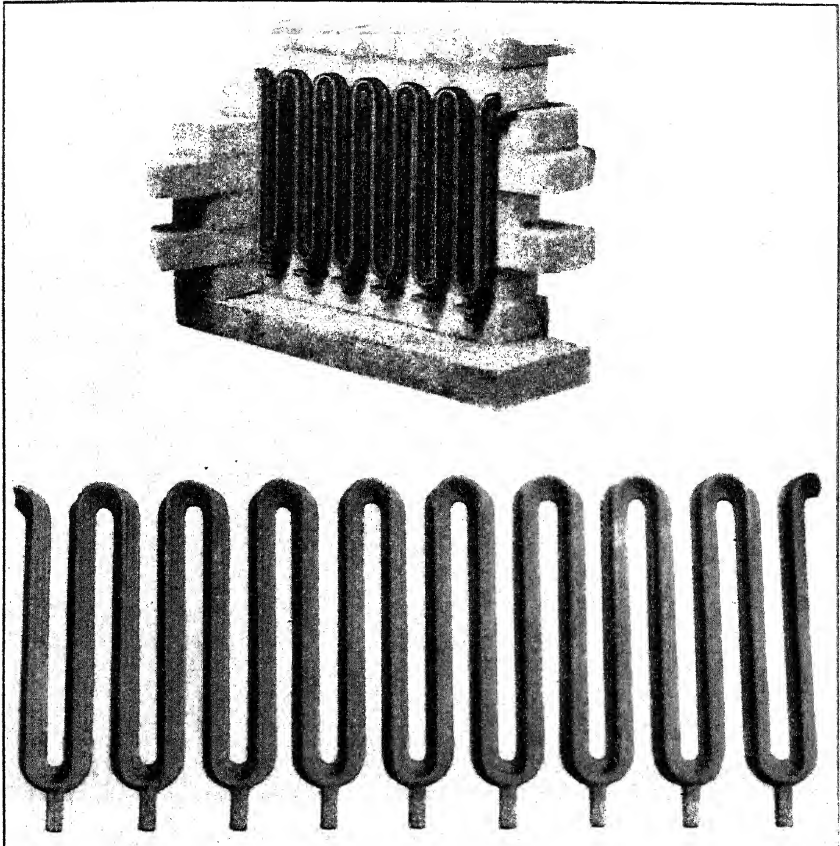


FIG. 113.   Cast Grid Type Furnace Resistor.

chromium resistors in their present stage of development, because in the case of the granular carbon resistors the temperature control and furnace efficiency is not so good, and the maintenance cost of the silicon carbide resistor is considerably higher than that of the nickel-chromium resistor at low temperatures.

*Resistance Heating Temperature Control.* — The present extensive application of resistor heating in industry results largely from the effect of the ease of temperature control on overall production costs. Automatic temperature control should be installed on most electric ovens and furnaces because of the following advantages in comparison with hand control:

    (1) Lower power consumption,
    (2) Lower labor cost,
    (3) Higher rate of production,
    (4) Easy duplication of results,
    (5) Less danger of failure of the heating element.
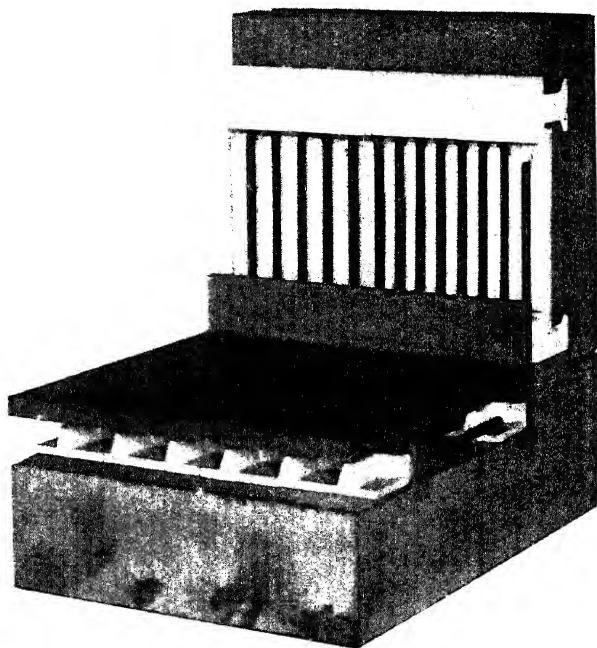


Fig. 114.   Wire or Rod Type Furnace Resistor.

Automatic temperature control for oven and heating operations up to 750° F. (399° C.) usually consists of a thermostat, a magnetic contactor panel on which the necessary relays and fuses are mounted, a disconnecting switch and a push button station. For higher temperatures a control pyrometer is used instead of

the thermostat. This system of control is the "on and off" method, that is, all of the heaters are either on or off. An oven or a furnace may have a number of control circuits, depending on the heat distribution desired. In the case of a furnace, there may be a gold fuse set in the furnace and connected in the control circuit so as to open the power circuit in case a thermocouple fails.

*Induction Furnaces and the Rocking Arc Furnace.* — Four types of induction furnaces are in use for metal melting. Two of these, the vertical ring and horizontal ring furnaces, operate on ordinary or low power frequencies, the former on 25 or 60 cycles, and the latter on 15 cycles. These types consist essentially of an electric transformer having a short circuited secondary winding usually of one turn, which becomes strongly heated when an alternating current is supplied to the primary winding. The secondary winding consists of a ring of molten metal in a re-fractory channel, horizontal in the case of iron or steel, but vertical for brass or non-ferrous metals. The heating takes place in this ring of molten metal, where the electrical energy induced in it from the primary winding is converted directly into thermal energy due to the resistance of the metal to current flow. In order to secure sufficient heating to keep the ring molten and to melt cold metal as added, the flow of current must be very high, as metals have a low resistance to passage of current. For example, assume that the primary winding of a 100 kilowatt induction furnace has 22 turns and is connected to a 220 volt alternating current circuit. At 100 kilowatts load the current in the primary is 454.5 amperes. Disregarding the transformer efficiency which is high, 97 per cent, power output is equal to power input. The secondary voltage is proportioned to the number of turns, so that with a primary winding having 22 turns and a secondary winding with one turn, the voltage induced in the secondary is 10 volts. The current, however, is inversely proportioned to the number of turns, so that the current in the secondary is 10,000 amperes, and it is from the passage of this high current that the heating results.

The horizontal ring furnace has a limited use for production of very low carbon steels and nickel-chromium alloys, because its operating cost is much higher than that of the arc type steel melting furnace. The vertical ring induction furnace is used for melting 90 per cent of the rolling mill brass and non-ferrous alloy production of the United States because the lower volatilization

of zinc makes the overall cost lower than fuel melting. It is doubtful whether either type will ever be extensively applied in the chemical industry.

*High Frequency Furnace.* — A third type of induction furnace, now of considerable importance for melting of metals on a production scale is the high frequency or iron-free induction furnace. In this furnace a crucible is heated by the eddy currents set up from a water cooled coil surrounding it, which is connected to a high frequency power circuit. The larger production furnaces operate on a frequency of 480 to 2000 cycles. The high frequency induction furnace has been used on a production scale for metal melting only a few years. Its development is in its infancy. The high frequency furnace is comparatively expensive to install, because of the electrical equipment required to produce high frequency current and because static condensers must be used to correct the low power factor of the furnace.

*Rocking Arc Furnace.* — Within recent years the rocking arc furnace has been widely applied in the brass foundry where it is more adaptable than the vertical ring induction furnace, because it is not necessary to maintain molten metal in the furnace 24 hours per day. It consists of a horizontal drum with two carbon electrodes projecting through the ends, a horizontal arc being drawn. The furnace is rocked through 180 degrees to prevent volatilization of zinc and fusing of the lining. About 15 years ago the technical procedure for production of barium oxide from barium carbonate was developed in a similar furnace which revolved through 360 degrees. The reaction involved is:

$$BaCO_3 + C = BaO + 2CO.$$
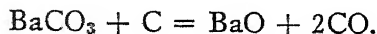
Barium oxide for desugarizing beet molasses is being made in one Italian [19] plant by this method, but an ingot furnace of the "series" type is used. The electric furnace process has proven the cheapest method of production of barium oxide.

### PROBLEMS

43. Calculate the theoretical power consumption in kilowatt hours for the production of 2000 lbs. of calcium carbide from pure lime and carbon, assuming that the carbide is tapped at 2000° C., and that the gases leave the furnace at 1000° C. (See Richards — Metallurgical Calculations.)

[19] H. W. Dahlberg. Barium Process Shows Interesting . . . for Desugarizing Beet Molasses, Chem. & Met. Eng., 31, 101 (1924).

44. What is the thermal efficiency of an 8325 kw. carbide furnace having a power consumption of 3300 K.W.H. per ton (2000 lb.) of carbide tapped?

45. Draw up electrical specifications for the purchase of a transformer suitable to supply the load of a 100 kw. single-phase arc furnace operating at 55 volts from a three-phase, 60 cycle, 13,200 volt circuit.

46. Determine the size of graphite electrode, and size of carbon electrode, which should be used on a 100 kw. single-phase arc furnace operating at 55 volts, both for round and square electrodes.

47. Calculate the theoretical power consumption in kilowatt hours for the production of 2000 lbs. of carborundum from pure sand and carbon, assuming that the average temperature to which the carborundum is heated is 2100° C., and that the gases leave the furnace at an average temperature of 1200° C.

48. Calculate the theoretical power consumption in kilowatt hours for the production of 2000 lbs. of carbon bisulfide, assuming that it is formed at 20° C., and is vaporized at 100° C., and that 20 per cent of the sulfur charged is lost.

49. What is the thermal efficiency of a carbon-bisulfide furnace having a power consumption of 1000 K.W.H. per ton (2000 lb.) of carbon bisulfide produced?

50. At what price per K.W.H. must electric power be available to produce 100 lb. steam from 150° F. feed water in the electric boiler at the same cost per 1000 lbs. of steam as it can be made in the coal fired boiler with coal at $5.00 per ton (2000 lb.)?

# CHAPTER X

## CATALYTIC PROCESSES

P. H. EMMETT, Ph.D.

**Introduction.** — Nearly 100 years ago Berzelius for the first time recognized in a series of reactions that had accumulated since earliest times the presence of a distinct and powerful force which he termed a "catalytic force."

In the years following the classification by Berzelius of the then known catalytic processes, there ensued an era of systematic research during which it became apparent that far from being an infrequent phenomenon, catalytic action plays an important role in a remarkably large number of reactions. The consensus of opinion during this period is well summarized by the words of Ostwald that "There is probably no type of chemical reaction which cannot be influenced catalytically, and there is no substance, element or compound which cannot act as a catalyzer."

The dawn of the 20th century witnessed the first important industrial exploitation of catalytic processes. Reactions which in general had been recognized as theoretically possible from what we may term a thermodynamic standpoint, that is, from a consideration of equilibria involved — but which had not been caused to take place at appreciable rates owing to the inertness of the reacting constituents — were now recognized as commercial possibilities provided only that suitable catalytic materials could be found. A thorough search for efficient catalytic materials has accordingly been carried on; a search that in many respects resembles the early quest of the alchemists for the elusive philosopher's stone. So remarkable has been the success of the workers in this field that some of the most important chemical industries of today and those looming largest on the horizon of the future are those depending for their very existence upon catalytic processes of one kind or another.

**Modern Concepts of Catalytic Surfaces and Reactions.** — Berzelius in 1835 defined a catalyst as "a substance that by its

312

presence has the power to rouse latent affinities so that compound substances undergo interaction and a greater electrochemical neutralization occurs." Today this definition still prevails. A more accurate understanding of the nature of catalytic phenomena however can be obtained by enumerating briefly the principal properties of such materials.

1. A catalyst changes the speed of a chemical reaction without itself undergoing a change either in quantity or composition. The physical nature of the catalyst may, however, be greatly altered. In Fig. 115 the photographs of a platinum gauze before
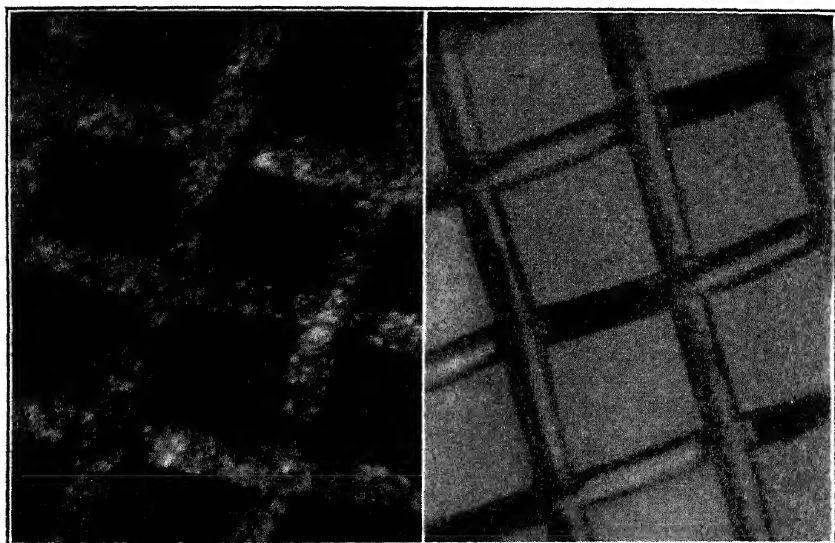


FIG. 115.  Pt-Rh Gauze Before and After Being Used 12 Hours for Oxidizing Ammonia.  (Photograph reproduced by courtesy of Mr. Yee of the Fixed Nitrogen Research Laboratory.)

and after use as a catalyst for the oxidation of ammonia show the pitting and marked alteration produced in the appearance of the surface of the catalytic material during use.   It is also true that occasionally a side reaction other than the main catalytic one gradually attacks and destroys, through chemical change, a catalytic material.   Thus, the sulfuric acid used as catalyst for the conversion of ethyl alcohol to ether is gradually reduced to sulfur dioxide which distils out of the reaction vessel.

2. Both positive and negative catalysts exist, the former accelerating and the latter retarding the rate of chemical reaction.

3. The equilibrium of a chemical reaction is not shifted by the presence of a catalytic material. Thus, hydrogen iodide if placed in a reaction vessel at 300° C. will, if left sufficiently long, attain the same percentage decomposition that would be reached in the presence of some catalytic material such as platinum. The catalyst merely shortens the time required to reach equilibrium.

4. Foreign substances when added to catalytic materials may either increase or decrease the activity of the latter. If such impurities increase the activity, they are called promoters; if they decrease the activity they are called poisons. Both poisons and promoters are, as we shall presently see, of fundamental importance in the commercial exploitation of any catalytic reaction.

5. Catalysts are usually very specific in their activity. Some progress has been made in classifying catalysts according to the types of reactions that they promote, but at present numerous exceptions occur in any such classification of catalytic materials. Examples illustrating the selective nature of many catalytic reactions will be considered in connection with certain industrial processes.

6. Very minute amounts of catalysts often are able to exert enormous catalytic effects. Thus Titoff found that the presence of a 0.0000000000001 N. copper sulfate solution is sufficient to produce a marked acceleration in the rate of oxidation of a solution of sodium sulfite.

**Industrial Utilization of Catalytic Materials.** — Catalytic processes have proved themselves a great economic advantage in industrial chemical undertakings. Their adaptation is usually for one of four purposes:

1. They are sometimes employed to speed up a particular reaction and probably in addition lower the temperature at which it will occur. They thereby effect a saving in time, in heat energy, and in general overhead expenses.

2. In many industrial processes purification of gases is carried out by rather complicated scrubbing in a number of different towers to remove first one impurity and then another. Often a suitable catalyst will permit the selective removal of the undesirable constituents of a gaseous mixture. Thus hopcalite, a

catalyst consisting primarily of $CuO$ and $MnO_2$, is able quantitatively to remove $CO$ from a gaseous mixture containing 99.0 per cent $H_2$, .5 per cent $CO$, and .5 per cent $O_2$, without burning any appreciable amount of the hydrogen present.

3. In organic preparations particularly, it is often desirable to produce a partial oxidation, that is, to permit oxygen to remove certain of the carbon or hydrogen atoms from an organic substance without completely burning the material to $CO_2$ and $H_2O$. Catalytic materials when appropriately chosen can effect such partial reactions in an almost quantitative manner.

4. Very indirect processes of preparing a particular substance can often be replaced by a direct catalytic process that will cause the constituents of the desired product to combine directly. The synthesis of ammonia from hydrogen and nitrogen over a suitable catalyst illustrates this type of industrial utilization.

Whichever of the above four possible functions a catalyst fulfills, it obviously effects a tremendous economic saving. Modern industry furnishes many instances in which the prices of products have been reduced enormously by the utilization of catalytic rather than non-catalytic processes in their manufacture.

In the following discussion of industrial catalytic processes, an endeavor will be made to indicate the general types of catalytic commercial processes now being used.

Catalytic reactions can be conveniently divided into four types:

1. Hydrogenation and dehydrogenation reactions, in which hydrogen is either added to or removed from some chemical substances.

2. Hydration or dehydration reactions involving the addition or removal of water molecules from one of the reactants.

3. Oxidation reactions.

4. General decomposition reactions that as a rule involve the splitting off of $CO_2$, $NH_3$, $SO_2$, or some other gaseous material. These four groupings include many important processes that are either being exhibited individually at present or that constitute potential commercial processes of the future. A few of these will now be briefly described.

By the use of finely divided nickel catalysts, hydrogen can be caused to combine with various unsaturated low-melting oils and to convert them thereby into high melting edible fats.

Nitrogen will, in the presence of iron catalysts at 450–700° C., combine with hydrogen to form ammonia. Promoted $ZnO$ catalysts will cause $H_2$ to combine with CO to form methyl alcohol, commercially known as "methanol." The catalytic hydrogenation of coal to form "synthol" and other possible motor fuels, is now being developed in Germany. These are only a few of the almost innumerable commercially important catalytic hydrogenation reactions that are being carried out today. Other hydrogenation or dehydrogenation catalysts are Co, Cu, MnO, MgO, Pd, Ir and Os.

Dehydrating catalysts for accelerating the rate of removal of water molecules from many organic compounds are extensively used. The best dehydration catalysts are $ThO_2$, $Al_2O_3$, and the blue oxide of tungsten, $W_2O_5$. Other oxides, including $Cr_2O_3$, $SiO_2$, $TiO_2$, $ZrO_2$, $Mo_2O_5$, $Fe_2O_3$, and $V_2O_3$, are also quite effective. This latter group of oxides, however, usually produces some splitting off of hydrogen in addition to causing the elimination of water molecules. Under certain special conditions of temperature, ordinary dehydrating agents such as $P_2O_5$ or $H_2SO_4$, as well as the anhydrous chlorides of Al, Fe and Zn, will act catalytically.

A few of the commercially important catalytic dehydrating reactions are:

$$2C_2H_5OH = C_2H_5OC_2H_5 + H_2O,$$
ethyl alcohol            ether

$$C_2H_5OH = C_2H_4 + H_2O,$$
ethyl alcohol        ethylene

$$C_2H_5OH + CH_3COOH = CH_3COOC_2H_5 + H_2O.$$
ethyl acetate
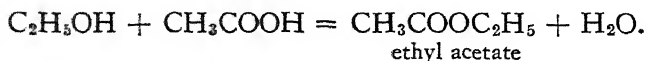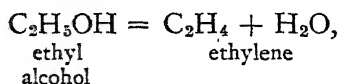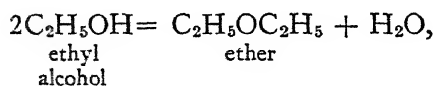
Oxidation reactions constitute perhaps the biggest and most important field of industrial catalysis. Such reactions divide themselves naturally into three classes: Complete oxidation reactions, partial oxidation reactions, and selective oxidation reactions. In the first class are included those processes in which catalysts are used to oxidize an element or compound to the highest possible state of oxidation, typical reactions being:

$$2SO_2 + O_2 = 2SO_3, \tag{1}$$

$$4NH_3 + 5O_2 = 6H_2O + 4NO. \tag{2}$$
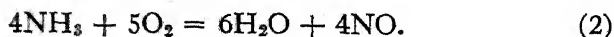
Probably the best general catalyst for complete oxidation reactions is Pt. It is so active that it is the most generally used catalyst for both reactions (1) and (2) above, in spite of its cost.

Other catalysts for complete oxidations include the remaining metals of the Pt group, namely: Ir and Os, and the oxides of Fe, Co, Ni, Cr, Cu, Mn, Ag, and Ce.

Partial oxidation refers to the oxidation of a compound to one of the lower state of oxidation without carrying it clear through to the final possible oxidation products. Such reactions are of particular importance in organic chemistry in which it is often desirable to oxidize a part of a molecule without converting the entire substance into $CO_2$ and $H_2O$. It has been found possible to bring about such a result by using oxidation catalysts that are less active than those mentioned above and accordingly are capable at proper rates of passage of the reacting mixture over the catalyst to produce the desired products. Thus, by the use of $V_2O_5$ as catalyst, naphthalene can be partially oxidized to phthalic anhydride, at temperatures between 320 and 330° C. Complete combustion of the naphthalene to carbon dioxide and water does not become appreciable under 400° C. with this catalyst. Other commercially important reactions of this type include the partial oxidation of toluene vapor to benzaldehyde, benzoic acid and anthraquinone, of alpha nitronaphthalene to phthalimide, of benzene to maleic acid, and of methane to formaldehyde. Many of these reactions are used on a commercial scale at present while others, though entirely workable on a laboratory scale, have not been found commercially profitable at present. Other partial oxidation catalysts include $MoO_3$, $WO_3$, $UO_3$, $As_2O_3$, $B_2O_3$ and $P_2O_5$.

Catalytically it is possible to bring about what has been termed selective oxidation. Such processes consist in the burning of one of the combustible constituents of a gas without burning others that are present. In the purification of hydrogen to be used for ammonia synthesis, for example, it is desired to burn out the 0.5 to 2.0 per cent CO present without burning any of the hydrogen. It has been found possible, at least on a laboratory scale, by the use of a "hopcalite" catalyst consisting principally of mixtures of CuO and $MnO_2$, to remove completely the CO by admitting about 2 per cent oxygen to the CO-$H_2$ mixture and passing these three gases together with a considerable amount of steam over the hopcalite. The steam serves to

prevent overheating and reduction of the catalyst. Under properly controlled conditions practically no hydrogen is consumed.

A great many useful but as yet for the most part not commercially exploited reactions consist in the elimination of $CO_2$, $H_2S$, $HCl$, $NH_3$ or $N_2$. For these decompositions for the most part very specific catalysts are necessary. The first three mentioned are carried out quite successfully by certain carbonates, sulfides and chlorides, respectively. Other useful catalysts for reactions of this type include Cu, Ni, Pt, MnO, $TiO_2$, ZnO, $Fe_2O_3$, CdO and $Li_2CO3$.

Since the rate of reaction is of primary importance from an economic standpoint in any commercial process, catalysts are of very great importance. If it is desired to speed up a reaction, a catalyst can usually be found. If it is essential to prevent the decomposition of some valuable product, negative catalysts are often available that will slow down many hundred fold the rate of the particular reaction involved.

**Catalytic Synthesis of Ammonia.** — An adequate idea of the chemical engineering problems involved in commercial catalytic processes can perhaps best be obtained by following through rather completely some particular industrial development, summarizing the obstacles that have had to be overcome by research, and pointing out the manner in which the various difficulties have been solved and the process brought to a commercial success. Perhaps no industrial exploitation of a chemical process has received more intense study and research in many years than has the production of synthetic ammonia. The problems confronting those responsible for bringing the process to its present state of development have been manifold and certainly include almost every type of difficulty that is likely to be met with in any such undertaking. Accordingly, the remainder of the present chapter will consist of a short but fairly comprehensive resume of the catalytic synthetic ammonia process — its inception, its struggles, the gradual surmounting of obstacles and its present status as a world-wide industry.

*Development.* — To appreciate fully the story of synthetic ammonia we must go back to a few of the historical high-spots of the present industrial development. As late as 1881 Graham-Otto states in his "Handbook of Inorganic Chemistry" that

nitrogen and hydrogen cannot be combined either under pressure, or by heat, or by the action of spongy platinum. Until that time it seems no one had succeeded in producing traces of ammonia by the direct combination of the two gases over a catalytic material. Soon, however, successful formation of traces of ammonia in a mixture of hydrogen and nitrogen was accomplished catalytically. Thus in 1884, Ramsay and Young passed a mixture of the two gases over a heated iron wire and detected traces of ammonia in the exit gas. Various other successful syntheses are recorded in the patent literature until finally in 1901, Le Chatelier, recognizing that to produce ammonia commercially by the reaction,

$$3H_2 + N_2 = 2NH_3,$$
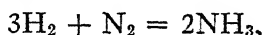
it was necessary to employ high pressure, succeeded in producing synthetic ammonia by the high pressure combination of the gases passed over a suitable catalyst (Fig. 116). Unfortunately the occurrence of a severe explosion wrecked his apparatus and deterred him from further high pressure experiments.

Haber and his students in 1904 took up the investigation of the high pressure synthesis of ammonia and finally in 1913, on behalf of the Badische Anilin and Soda-Fabrik and in cooperation with Bosch, who had developed successful methods of preparing and purifying the huge quantities of gas needed, and had overcome the engineering difficulties of carrying out the reaction at high temperatures and pressures, brought the work to a successful conclusion. Some 500 tons of synthetic ammonia was produced by the Haber-Bosch process in 1913; today the yearly production of synthetic ammonia exceeds 1,000,000 tons. Thus a chemical reaction that only 48 years ago was believed not to be possible has been developed into one of the world's largest chemical industries. It stands indeed as a triumph to modern physical chemistry and chemical engineering.

The reaction $3H_2 + N_2 = 2NH_3 + 26,000$ calories, is exothermic, approximately 13,000 calories of heat being evolved per mol of ammonia at 600° C. Furthermore it involves a decrease of 50 per cent in the number of molecules present in the reacting system. Consequently, in accordance with the well-known principle of Le Chatelier, one would expect to find the most favorable equilibrium condition for the reaction at low temperature and high pressures. That such is actually the case is

evidenced by the curves as given in Fig. 116 which are based upon equilibrium determinations made at the U. S. Fixed Nitrogen Research Laboratory, in Washington, D. C.
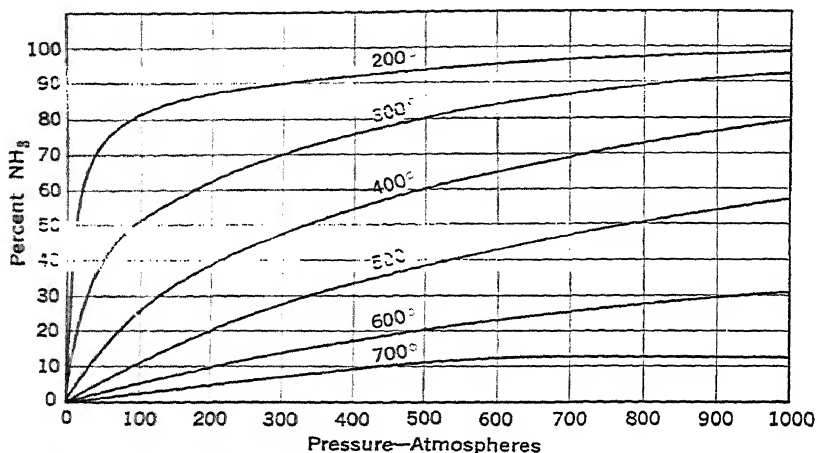


FIG. 116.   Per Cent Ammonia Formed from $3H_2 + N_2$ at Equilibrium at Various Temperatures and Pressures.

*The Search for a Catalyst.* — To cause a mixture of hydrogen and nitrogen to combine sufficiently rapidly and at a low enough temperature to be of use from a commercial point of view, active catalysts must be employed; furthermore, to enable full advantage to be taken of the increase in the equilibrium per cent of ammonia obtained by high pressure, the engineering difficulties attending the use of such pressures must be overcome.   These two problems then, that of suitable catalyst development, and that of adequate engineering design of reaction bombs to stand the high pressures and temperatures needed for the process, together with the difficulties involved in the preparation and purification of the hydrogen and nitrogen needed in the reaction constitute the principal difficulties that have to be overcome in the successful commercial processes.

The search for suitable catalytic materials has led to the inclusion of almost every element of the periodic table in patents for synthetic ammonia production.   An early group of patents included the metals Bi, W, Ir, Rh, $Hg_2Cl_2$, Os, U, Fe, Ni, Co, Pt, Mo, Mn, Cu, Ag, and Zn.   An Fe-Mo catalyst consisting largely of iron with a few per cent of Mo, was early used by the first

Haber-Bosch process. Later, however, the use of Fe promoted with $Al_2O_3$, $SiO_2$, $ZrO_2$ or similar material was patented. This gradually became the most used catalyst in European plants. During the period 1918–1925 work at the F.N.R.L. has led to the development of a still further improvement in the Fe catalyst by promoting it both with an acidic oxide such as $SiO_2$, $ZrO_2$ or $Al_2O_3$, and a basic oxide such as $K_2O$ or $Na_2O$. (This doubly promoted catalyst is usually called the Larson catalyst.) When operated on pure 3 : 1 hydrogen-nitrogen gas, this type of doubly promoted catalyst is definitely superior to a catalyst promoted by only $Al_2O_3$. It is a rather peculiar fact that the addition of $K_2O$ alone to pure Fe definitely decreases the activity of the latter, producing a catalyst markedly inferior to pure Fe. Nevertheless the addition of $K_2O$ to a catalyst already promoted with $Al_2O_3$ produces a still further improvement in catalytic activity. The relative efficiencies of pure iron, as compared to that promoted with $K_2O$ alone, $Al_2O_3$ alone, or both $Al_2O_3$ and $K_2O$, can be judged by Table I. The singly or doubly promoted iron catalyst is at present the principal one used in industry.

TABLE I. — TEMPERATURE 450° C., SPACE VELOCITY 5000 *

| | *Per Cent Ammonia* | |
| Promoters | 80 Atm. | 100 Atm. |
|---|---|---|
| 1.01 per cent $Al_2O_3$ | 5.02 | 9.00 |
| 0.35 per cent $K_2O$ + 0.84 per cent $Al_2O_3$ | 5.82 | 13.60 |
| 0.61 per cent $ZrO_2$ | 4.88 | 7.72 |
| 0.96 per cent $K_2O$ + 2.76 per cent $ZrO_2$ | 5.43 | 12.73 |
| 0.51 per cent $SiO_2$ | 4.67 | 7.49 |
| 0.57 per cent $K_2O$ + 0.75 per cent $SiO_2$ | 5.33 | 10.90 |

Two characteristic and important properties of synthetic ammonia catalysts should be noted, namely, their behavior under the action of poisons and their efficiencies when operating under various pressures of 3 : 1 hydrogen-nitrogen gas. Poisons

* The term space velocity as used in the above table and as current in catalytic literature is defined as "the number of liters of gas passing over a catalyst per liter of catalyst per hour." Thus a flow of 25,000 liters of gas per hour over 5 liters of catalyst is a space velocity of 5,000. Similarly, obviously 25,000 cc. of gas per hour or 417 cc. of gas per minute over 5 cc. of catalyst is equivalent to a 5000 s.v. The space velocity is usually defined in terms of the total exit volume of gas leaving the reaction bomb (calculated at 0° C. and 760 mm.). This is not the same as it would be were it calculated on the basis of the entering stream of gas in any case in which the reaction taking place involves a change in the total number of molecules in the system.

for the iron catalysts include oxygen containing compounds such as CO, $CO_2$, $H_2O$, $CH_3OH$, $O_2$, etc.    Most of these in the presence of high pressure hydrogen are hydrogenated to hydrocarbons and water.    Their poisoning action is proportional to the oxygen content.    $H_2S$, organic sulfides, and similar materials are also poisons for synthetic $NH_3$ catalysts.    Their effective removal is one of the problems that has to be solved in gas purification.

Promoted Fe catalysts for ammonia synthesis possess a marked pressure coefficient as far as catalytic activity is concerned. Those which are active at lowest pressure often are not so active
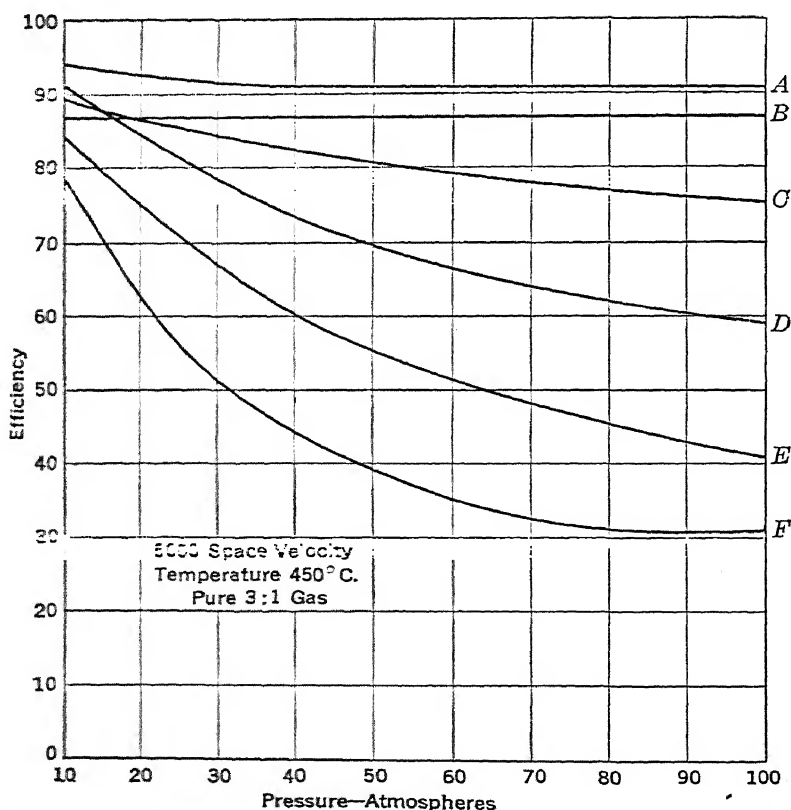


Fig. 117.   Effect of Pressure on Efficiency of Synthetic Ammonia Catalysts.

at higher pressures.   On the other hand, those catalysts that are not so active at low pressures may prove to be fairly efficient as

high pressure catalysts. Thus it becomes necessary to complicate the study of high pressure synthetic ammonia catalysts by testing them at several pressures, up to at least 100 atmospheres before one can be certain of their behavior under commercial operating conditions. A plot of the efficiency vs. pressure characteristics of several different catalysts is shown in Fig. 117. As a rule singly promoted catalysts have pressure coefficients that are markedly larger than those for catalysts containing both $K_2O$ and $Al_2O_3$. The mechanism by virtue of which $K_2O$ is thus able to cause an iron catalyst promoted with $Al_2O_3$ to maintain a high efficiency at high as well as low pressures is not clear. It is one of the many perplexing problems still unsolved in connection with the *modus operandi* of synthetic ammonia catalysts.

A convenient type of apparatus for testing catalysts at high pressure has been developed at the F.N.R.L. A cross section of the apparatus is shown in Fig. 118. In brief it consists in means for causing a stream of pure 3 : 1 hydrogen-nitrogen gas to pass over a catalyst held in a bomb at a definite temperature and pressure. For the full working details of such a catalyst apparatus, the reader is referred to a more elaborate description given in the literature.[1] The essential features of the diagram shown are self-explanatory.

*Preparation and Sources of Hydrogen.* — It has been estimated that the preparation and purification of hydrogen constitute about 75 per cent of the cost of manufacturing synthetic ammonia. Accordingly, a great deal of research has been carried out in an effort to develop means of obtaining a cheap supply of pure hydrogen. As has already been stated, synthetic ammonia catalysts are very susceptible to poisoning by small amounts of CO, $H_2O$, $O_2$, $CO_2$, $H_2S$, S and numerous other materials. Hence an unusually pure grade of hydrogen is essential for successful commercial production of synthetic ammonia.

The possible sources of hydrogen that have been of use commercially or promise to be of commercial importance in the future are as follows:

1. Water gas.
2. Coke oven gas.
3. Electrolysis of water.

[1] Larson and Brooks, Chem. & Met., **26**, 555 (1922).
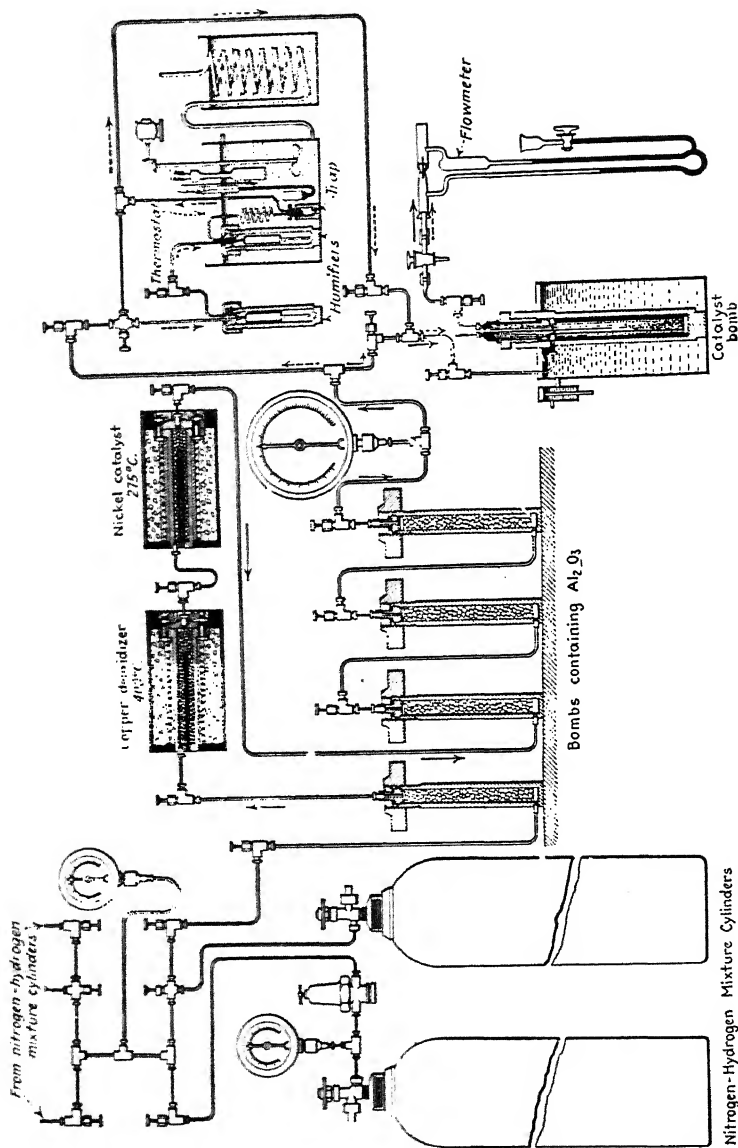
FIG. 118. Diagram of Complete Apparatus for Small Scale Testing of Ammonia Catalysts at Variable Pressure.

4. By-products from production of chlorine, fermentation processes, etc.
5. Steam-iron reaction.
6. Phosphorus-steam reaction.
7. Cracking of hydrocarbons, large quantities of which are present in natural gas.
8. Miscellaneous reactions such as sulfur-steam, or sinz blende-steam-air.

Of these, the first four are the only ones commercially utilized at present in the preparation of synthetic ammonia.

*Water Gas Hydrogen.* — Water gas is the name given to the gaseous mixture obtained by blowing steam over hot carbon, according to the reaction:

$$H_2O + C = CO + H_2. \tag{1}$$
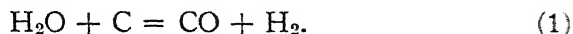
Its composition is approximately as shown in Table III.

The purification of water gas is carried out in one of two ways, which have become known as the catalytic and liquefaction processes, respectively. The first of these involves the catalytic conversion of CO into $H_2$ according to the reaction:

$$CO + H_2O = CO_2 + H_2 + 10,000 \text{ gram calories.} \tag{2}$$
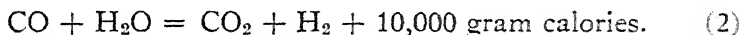
The latter involves the liquefaction of the water gas and separation of the $H_2$ and CO by fractional distillation. The several liquefaction processes are also used in connection with the purification of coke oven gas and will be discussed in connection with that second source of hydrogen.

About 70 per cent of the hydrogen for synthetic ammonia production is obtained by the water-gas catalytic process. Equilibrium conditions for reaction (2) above are given for various temperatures in the following table, where

$$K = \frac{P_{CO}P_{H_2O}}{P_{H_2}P_{CO_2}}.$$

*Removal of Impurities.* — Obviously the lower the temperature at which the gas mixture of steam, $CO_2$, $H_2$ and CO can be brought to equilibrium, the lower will be the per cent CO in the residual gas. Commercially, for the most part promoted iron oxide catalysts are used. These require for efficient operation a

TABLE II. — EQUILIBRIUM PER CENT OF CO IN CONVERTED WATER GAS
(After drying and removing $CO_2$)

| Temperature | Steam: water gas ratio | | |
|:---:|:---:|:---:|:---:|
| | 3 : 1 | 4 : 1 | 5 : 1 |
| 400° | .72 | .52 | .47 |
| 500° | 1.70 | 1.25 | .97 |
| 600° | 3.26 | 2.72 | 2.03 |
| 700° | 4.59 | 3.58 | 2.92 |
| 800° | 6.28 | 5.00 | 4.28 |

temperature of 450° to 500° C.   Under such temperature con-
ditions 2 to 4 per cent  CO is left in the gas after passage over the
catalyst.   The removal of the last small per cent of CO is an
expensive portion of the purification process.   Catalytically it
can easily be hydrogenated to $CH_4$, but this is undesirable since
the latter gas accumulates as an inert material in the circulatory
synthetic ammonia systems and necessitates frequent purging
however, with attendant loss of hydrogen and nitrogen.   At
present, in large scale hydrogen production, this final amount of
CO is removed from the hydrogen by a method involving scrub-
bing the gas with ammoniacal cuprous chloride, or still better
ammoniacal cuprous carbonate or formate containing excess of
ammonia.   Such scrubbing, coming as it does after high pressure
scrubbing with $H_2O$ for removing the $CO_2$, not only reduces the
CO to a few hundredths of one per cent but also eliminates oxy-
gen, the final traces of $CO_2$ and any $H_2S$ that may be present in
the gas.   The CO-cuprous complex, probably $Cu_2(NH_3)_{2n}CO_3 \cdot$
$2CO \cdot 4H_2O$, decomposes, evolving CO when heated in vacuo to
70° C.   The original scrubbing solution is thereby regenerated.
   The remaining impurity, water vapor, is removed by refrig-
eration at high pressure or by passage over soda-lime or sodamide.
In many plants a final clean-up of the gas is effected by passing it
over two or three preliminary ammonia catalysts that form suf-
ficient ammonia to act as an effective scrubbing agent when the
latter is condensed and the uncombined hydrogen and nitrogen
pass on to other converters.
   *Coke Oven Gas Hydrogen.* — The so-called liquefaction process
as applied either to water gas or coke oven gas is used in the
preparation of hydrogen for about 12 per cent of the present

synthetic ammonia production. It has been worked out in detail by Claude and is used in the Claude synthetic ammonia installations. Coke oven gas, having a composition approximately as shown in Table III, or water gas, is scrubbed free of most of the $CO_2$ at 25 atm. pressure over cold water. The last traces of this gas are removed by lime water, for otherwise it would by freezing later plug up the liquefaction system. On cooling the remaining gas, ethylene and the higher hydrocarbons, then methane, then CO, and finally nitrogen are liquefied out. The nitrogen, liquefying last, runs down the purifying column and dissolves out the last traces of impurities. The hydrogen thus obtained expands in an engine, thereby doing external work and cooling itself down to $-210°$ C. By heat interchangers this cool hydrogen cools incoming coke oven gas and assists in its liquefaction. Sufficient nitrogen remains in the hydrogen to condense as a liquid and serve as a lubricant in the expansion engine. The $H_2$ obtained is pure except for about 2 per cent CO which is removed by scrubbing as already described. The liquefied gases can be utilized in various ways. The ethylene may be converted into ethyl alcohol; the CO is either utilized in the making of methanol, absorbed in alkali to form sodium formate, or burned in furnaces for its heat content.

*Electrolytic Hydrogen.* — Electrolytic hydrogen is utilized commercially for the production of about 15 per cent of the world's supply of synthetic ammonia. The hydrogen obtained from a properly designed cell is very pure and is ideal for use. The principal drawback to the process is an economic one — power is expensive. Accordingly, only in Japan, Norway, some portions of Italy and France, and such places in the United States as have exceptionally cheap power, can electrolytic hydrogen be utilized for ammonia synthesis. As oxygen is produced simultaneously with the hydrogen, the cost of the latter will be materially reduced if a market can be obtained for the oxygen.

*Other Sources of Hydrogen.* — The remaining three per cent of the synthetic ammonia produced is obtained from by-product hydrogen. The electrolytic production of chlorine and of caustic soda furnishes considerable hydrogen. Hydrogen formed in a fermentation process for the formation of normal butyl alcohol is utilized in one plant in the United States for running a small synthetic ammonia unit.

The iron-steam process has for a number of years been the

means of manufacturing hydrogen for hydrogenation of oil and for other uses in which a very pure product is desired, but for economic reasons it has not been employed in the synthetic ammonia industry. The cracking of hydrocarbons, such as methane, catalytically or otherwise has been accomplished on a laboratory scale, but is not at present being used for commercial hydrogen production.

The possibility of producing hydrogen by the reaction:

$$P_4 + 10H_2O = 2P_2O_5 + 10H_2,$$
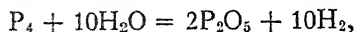
is one of the most promising for industrial utilization. A great deal of work is now being carried out in an endeavor to extract P from phosphate rock by various blast furnace reduction processes. Once this is placed on a commercial basis, the commercial production of both phosphoric acid and hydrogen by the above reaction seems eminently probable. Such a process has already been patented by Liljenroth.

*Preparation of Pure Nitrogen.* — The nitrogen is obtained either directly or indirectly from the air. Its separation from oxygen by the direct method involves the liquefaction and fractional distillation of air. The Pictet process, later modified by Claude, enables one to obtain a remarkable separation of oxygen and nitrogen with great economy of power. Air, cooled by heat interchangers and by expansion, is admitted to the base of a column down which liquid nitrogen is permitted to flow. This effects a fractionation of the air, the oxygen dissolving in the descending stream of liquid, while the nitrogen having the lower boiling point volatilizes and passes off at the top of the column. This process necessitates the actual liquefaction of only about 1/5 of the total nitrogen prepared and thus effects a great saving in power. Nitrogen for most of the Claude installations is obtained by such a liquefaction process. The nitrogen obtained by this or other methods from the air contains about one per cent of argon and other inert gases. As these gases do not enter into the ammonia reaction and are not removed in the scrubbing process they tend to accumulate in the nitrogen fixation system. Unless there is considerable leakage, purging or blowing off is necessary to eliminate these gases.

The indirect methods of obtaining nitrogen from the air depend upon removing oxygen by combustion. If a sufficiently large and cheap supply of hydrogen is available, as for example in

localities abounding in power sufficiently cheap to permi the use of electrolytic hydrogen, oxygen may be burned economically by hydrogen. A suitable stream of air and electrolytic hydrogen burned in appropriate mixtures thus results in the complete removal of oxygen and yields a gas containing the desired 3 : 1 ratio of hydrogen and nitrogen. Some argon, of course, will remain as a diluent. Such a process is utilized by the Fauser modification of the Haber process.

When electrolytic hydrogen is not available and water gas hydrogen is resorted to, many industrial concerns have found it best to obtain the desired supply of nitrogen by mixing water gas with a suitable amount of producer gas. The usual composition of the two gases is shown in Table III. The

TABLE III. — COMPOSITION OF GASES UTILIZED IN THE SYNTHETIC AMMONIA INDUSTRY

|  | Coke Oven Gas | Producer Gas | Water Gas | Mixture of Producer and Water Gas |
|---|---|---|---|---|
|  | per cent | per cent | per cent | per cent |
| Carbon dioxide.................... | 5 | 5 | 2–6 | 3–5 |
| Carbon monoxide................. | 3 | 25 | 40–45 | 35–40 |
| Hydrogen........................ | 50 | 5 | 49–51 | 33–36 |
| Nitrogen........................ | 15 | 63 | 0–2 | 22–23 |
| Methane......................... | 24 | Traces | 0 | Traces |
| Inert gases (Argon, etc.)............ | 3 | 2 | 0 | 1 |

composition of the gas obtained by mixing the two gases in suitable amounts is given in column four. Removal of the carbon monoxide is then effected in the manner described above for its elimination from water gas in the production of pure hydrogen. By this method the carbon monoxide is converted to carbon dioxide with the production of an equal volume of hydrogen. This is the source of nitrogen and hydrogen for the Oppau and Merseburg synthetic ammonia plants in Germany, which together produce about 70 per cent of the world output of synthetic ammonia.

*Ammonia Synthesis.* — Numerous modifications of the original Haber-Bosch process for producing synthetic ammonia have appeared in the patent literature from time to time. Some of these have differed sufficiently from the original process to

enable their inventors to obtain patent rights on new processes for producing synthetic ammonia. Thus the Casale, Claude, Fauser, General Chemical Company, American, and Mont Cenis "processes" have sprung into existence. In the course of the present discussion no attempt will be made to describe each of these in detail. Instead, a general presentation of a number of the characteristics fundamental to all synthetic ammonia processes will be made. Finally, a fairly complete and detailed explanation will be given of the Haber-Bosch process as it exists today and of the Claude process, which perhaps is the most radical departure in design and detail from the original installation.

As has already been pointed out, equilibrium conditions for the formation of ammonia from hydrogen-nitrogen mixtures are such as to make it desirable to operate at as high a pressure and as low a temperature as practicable. The upper limit of the commercially practicable pressure range is determined by various engineering difficulties involved in the safe compressing and handling of the reacting gases at high temperatures. The lower limit of temperature is governed by the activity of the catalyst used and the purity of the gas obtainable. In practice, pressures ranging from 100 to 1000 atmospheres and temperatures varying from 475° C. to 650° C. or higher are employed.

*Ammonia Converters.* — One of the most difficult and yet the most important part of every synthetic ammonia process is the design and construction of the reaction bomb. The material of which this is constructed must resist very high pressure at relatively high temperatures and must also be resistant to disintegration by the mixed gases as well as the ammonia. A tremendous amount of research has been and is still being carried out for the purpose of finding steels that retain high tensile strength at a red heat and that are not badly weakened by the prolonged action of hydrogen-nitrogen-ammonia mixtures. In general, alloy steels containing little if any carbon, are utilized. Chromium, tungsten and vanadium steels, containing also usually some nickel, are reported by the Badische patents to be extremely serviceable. As a result of tests at the Fixed Nitrogen Research Laboratory a chrome-vanadium steel in which the ratio of carbon to chromium is not greater than 1 to 8, is recommended. In addition to those mentioned above, nickel-chromium alloys commercially known as nichrome, are used. Also a

French steel known as A.T.G. is supposed to possess the desired characteristics to a remarkable extent, as is also an even more recently developed product manufactured by Messrs. Vickers of Sheffield, England, and known as "Vichronic."

It was soon realized that even the best available steels would not long withstand the action of high pressure hydrogen, nitrogen, ammonia mixtures if heated externally to the red heat necessary for efficient operation of the catalyst. Hydrogen, particularly, was found to attack and cause rupture of steel, presumably as a result of its hydrogenating the carbon content of the reaction bomb to methane. Consequently, bombs have been designed in such a manner as to prevent the outside pressure resisting shell from attaining the high temperature reached by the catalytic material. Furthermore, since the combination of nitrogen and hydrogen to form ammonia is strongly exothermal, care must be taken to prevent the development of hot-spots at the point at which the fresh hydrogen-nitrogen mixture first strikes the catalyst. Proper use of heat interchangers in all commercial converters has made the combination of the hydrogen and nitrogen autothermal, that is, capable of maintaining itself by the heat evolved during the reaction. In some of the reaction bombs employing extremely high pressures, dissipation of heat becomes quite a problem. All ammonia bombs are designed with a view of maintaining a constant temperature at or near 500–550° C. throughout. In the accompanying sketches, portions of different types of commercial reaction bombs are shown.

Figure 119 is a sketch of one of the bombs first used in the Haber-Bosch process. The pressure-resisting walls of the bomb, it will be noticed, are heavily insulated from the main catalyst chamber. The counter current circulating heat interchanger is also in evidence. A later designed bomb, a large model of which will be described in discussing the working details of the Haber-Bosch process, is shown in Fig. 120. A very efficient type of bomb designed by the F.N.R.L. is shown sketchily in Fig. 121. The stream of cool entering gas passes up along the side of the bomb in direct contact with the pressure-resisting wall. It then becomes heated in heat interchangers as shown, passes down over an auxiliary heater used for bringing the gases to the temperature necessary to start the reaction, and then into a series of three concentric cylinders containing the catalytic
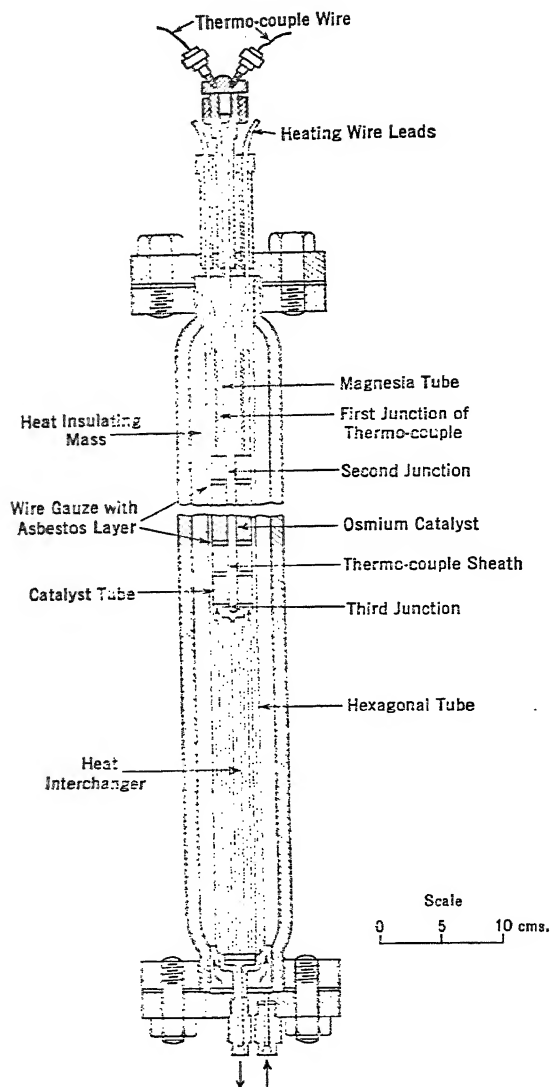
FIG. 119.  Early Type Haber-Bosch Bomb.

material. These vary in size in such a way that the fresh ammonia free gas strikes that portion of the catalyst contained in the smallest of the three annular spaces and hence passes through the catalyst most rapidly. The second annular space is larger than the first, and the third still larger. Thus the gas velocity gradually decreases as the percentage of ammonia increases. Since the presence of ammonia retards the rate of combination of hydrogen and nitrogen, a slower rate of flow with increased ammonia content is desirable in order to distribute the formation of ammonia and hence the generation of heat smoothly over the entire catalyst.

The super pressure Claude bomb is very simple in design, as shown in Fig. 122. The heat insulating material designed to retard the loss of heat is thickest at the point at which least heat is being generated.

*Removal of Ammonia.*—The methods of separating the ammonia formed in any particular process consist either in the condensation of anhydrous ammonia by cooling the high pressure gases leaving the converters, or in the absorption of the ammonia by scrubbing with water. The choice between these two possibilities depends upon the per cent ammonia present in the exit gas from the converters and the pressure used in the synthetic process. In those processes in which the operating pressure is 200 atmospheres, as in most of the Haber modifications, and the exit gases contain only 5 per cent to 7 per cent ammonia, water scrubbing is resorted to as the most economical means of separating ammonia from the effluent hydrogen-
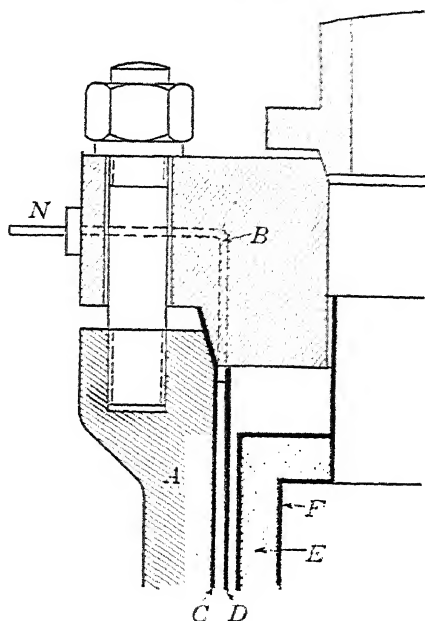


FIG. 120. Section through Latest Haber-Bosch Bomb.

*A*—Steel shell; *B*—Lid; *C*—Feed tube; —*D* Steel tube; *E*—Insulating layer; *F* —Iron catalyst tube; *N*—Tube admitting nitrogen.

Fig. 119. Early Type Haber-Bosch Bomb.

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Gas Outlet

Pyrometers

Heat Interchangers

Heating Element

Catalyst Space

Gas Inlet

FIG. 121.   Bomb Designed by the Fixed Nitrogen Research Laboratory.

nitrogen mixture. Usually 25 per cent aqueous solutions are thereby obtained. In processes such as that designed and operated by Georges Claude, in which super-pressures of 1000 atmospheres are used and the ammonia conversions reach as much as 40 per cent, condensation of the ammonia by refrigeration is found to be practicable. In fact 97 to 98 per cent of the $NH_3$ in the exit gas from such a Claude unit condenses at room temperature. A pure anhydrous product is thereby obtained.

The various processes for producing synthetic ammonia usually arrange the high pressure converters either in parallel, or in a combination of the series-parallel arrangements. In general, those processes in which the conversion per passage is only 7–9 per cent adopt a circulating system by which the exit gas from a bomb or from a number of bombs in parallel is scrubbed free of ammonia, and the gas, together with a sufficient additional amount of hydrogen and nitrogen to take the place of the ammonia formed, is recirculated by a pump over the catalyst again.

This is the arrangement adopted in the modern Haber process. On the other hand, if extremely high pressures are being used, as in the Claude process, such that at a single passage of the gaseous mixture over the catalyst as much as 40 per cent of the hydrogen and nitrogen can be converted



FIG. 122. The Claude Bomb.

*A*—Gas entrance; *B*—Entrance of gas into catalyst space *C*—Gas exit; *E*—Insulating layer; *M*—Shell; *T*—Headpiece.

into ammonia, it is found most economical to employ two bombs in parallel, followed by a like number in series, the ammonia being scrubbed out between each set of bombs. The final unconverted mixture is not recirculated at high pressure but is expanded to one atmosphere and run back into the nitrogen-hydro-

gen supply or burned under boilers —whichever at the moment may be the more advantageous.

*Haber Process.* — Most of the essential features of the Haber process have already been pointed out. In Fig. 123 is shown
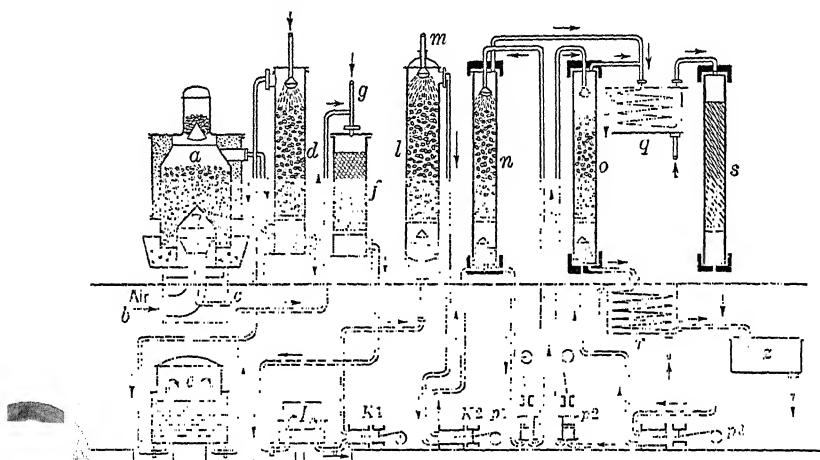


FIG. 123.    The Haber-Bosch Process.

*a*—Rotating water gas generator; *b*—Air entrance; *c*—Steam entrance; *d*—Gas purifier; *e*—Gasometer for water and producer gas; *f*—Water gas converter; *g*—Steam entrance; *I*—Gasometer for converted gas; $K_1$—Compressor to 25 atm.; $K_2$—Compressor to 200 atm.; *l*—Carbon dioxide purifier at 25 atm.; *m*—Scrubwater; *n*—Carbon monoxide purifier at 200 atm.; *o*—Ammonia absorber; $p_1$—Liquid pump; $p_2$—Water pump; $p_3$—Circulating pump, 200 atm.; *q*—Gas cooler; *r*—Water cooler; *S*—Ammonia converter; *Z*—Ammonia water.

diagramatically a complete Haber unit. In the large rotating furnace "*a*," water gas is produced by blowing steam through the entrance over hot coke or, as is more recently done, over lignite. Then the gas proceeds through a purifier "*d*," in which dust particles are washed out, through gasometer, "*e*," catalyst container, "*f*," for converting the CO-steam mixture into $CO_2$ and $H_2$, and another gasometer, "*I*." By compressor $K_1$ the gas is compressed to 25 atmospheres and the $CO_2$ scrubbed out with water in tower "*l*." Pump $K_2$ boosts the gas pressure to 200 atmosphers, after which in tower, "*n*," the CO remaining from the catalytic conversion in chamber "*f*," is removed by ammoniacal cuprous solutions as already described. After passage through a water cooler "*q*," as a means of condensing

out all of the excess moisture, the gas is ready for passage into the high pressure catalyst bomb at "*s*." The ammonia formed is absorbed in tower "*O*" and the unconverted hydrogen and nitrogen permitted, as shown, to join the incoming fresh hydrogen-nitrogen mixture.

A similar set-up is used in the American modification of the Haber process, known as the "American Process." The circulation of the gases can be traced in this case with the help of Fig. 124. Hydrogen from a series of electrolytic cells or from any other source after being purified is passed through a burner by which the hydrogen is burned in air to remove the oxygen and to furnish the necessary 3 : 1 mixture. The desired mixture of nitrogen and hydrogen is then compressed, circulated through a series of oil traps, then a preliminary purifying bomb and finally through a bank of three converters operating in parallel. The remainder of the hydrogen-nitrogen mixture, that is, the portion not converted into ammonia, is, after removal of the ammonia in the condensers, sent back into the supply of high pressure 3 : 1 gas. A feature of this process is a circulating pump lubricated by liquid ammonia for the purpose of avoiding contaminating the gas with oil spray and vapors that result in ordinary types of pumps lubricated with oil.

A good idea of the construction of a commercial Haber converter can be obtained from Fig. 120, and a description of the apparatus. The converter of a unit producing 20 tons of ammonia per day consists of alloy steel tubes $A$, 12 meters long, in two flanged 6 meter sections, bolted together. The internal diameter is about 80 cm. and the metal 18 cm. thick. Fitting internally is a pure iron liner $C$, 12 mm. thick, which protects the outer casing from the action of the hot compressed reducing gases. This liner makes gas-tight joints with end caps that are securely fastened with 15 four-inch iron studs. The outer casing of the bomb is perforated with small tapering holes which permit the escape of any gas diffusing through the inner liner and hence prevents the building up of pressure between the outer wall $A$ and the iron liner $C$. On the inside of the tube $C$ there is a concentrically placed steel tube $D$ which is held by rings at a distance of 1–2 cm. from $C$. Through the space between these tubes nitrogen is led by the tube $N$. The pressure of nitrogen is of course equal to the total pressure within the catalyst bomb itself. The blanketing atmosphere of

Electrolytic Cells

Hydrogen Gasometer

Hydrogen Blower

Burner    Air Blower

$N_2 + 3H_2$ Gasometer

Compressor

Oil Traps

Purifier

H.P. Condenser

H.P. Receivers

Converter

Condensers

Circulating Pump

Condensers

H.P. Receivers

L.P. Receiver

Hydrogen ——→ 1
Air ——→ 2
$N_2 + 3H_2$ Gas ——→ 3
$NH_3 + N_2 + 3H_2$ Gas ——→ 4
$NH_3$ Liquid ——→ 5
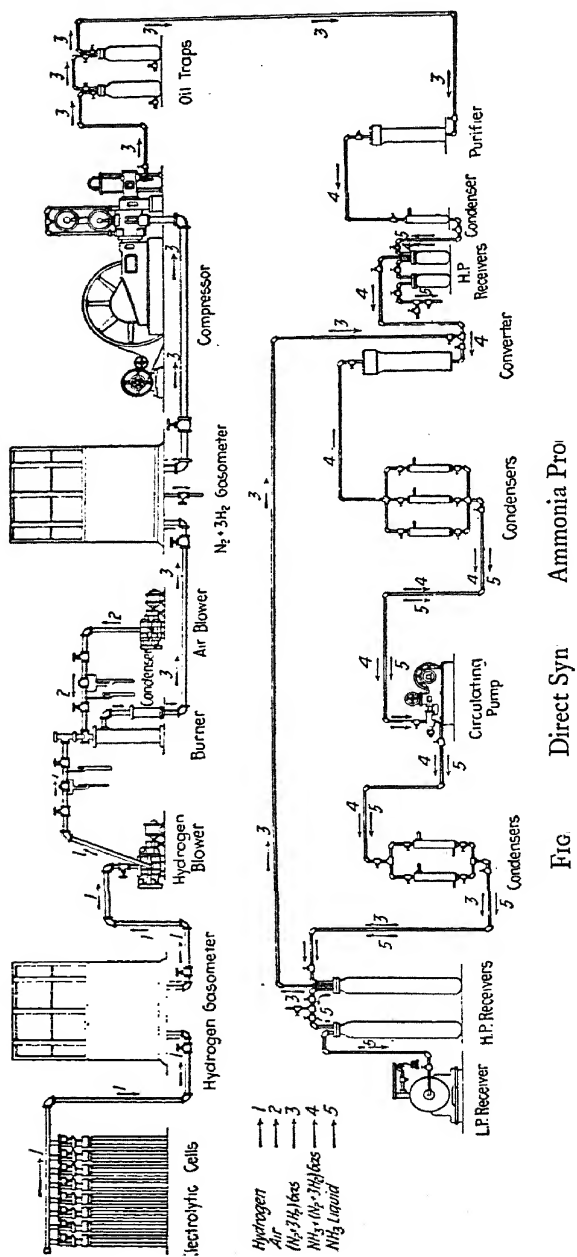
Fig.    Direct Syn    Ammonia Pro

nitrogen practically eliminates the destructive corrosion of the pressure resisting shell by hydrogen and is a pronounced safety factor insofar as it prevents the outward diffusion of hydrogen through the sides of the converter. Finally, there is the iron tube $F$, concentrically placed to $D$, which holds the catalyst mass. It is surrounded by the insulating layer $E$. The remainder of the bomb contains essentially catalyst space, heat interchangers for distributing the heat evenly, and means of heating the catalyst sufficiently at the beginning of a run to start the formation of ammonia and thus heat the entire catalyst to a suitable temperature. The catalyst operates ·at about 600° C., whereas the outer casing does not rise above 300–400° C. Such a unit weighs approximately 70 tons. It requires several days to change the catalyst and restart the bomb.

*Claude Process.* — Perhaps the most distinct and complete departure from the original Haber process had been made by Georges Claude in the superpressure synthetic ammonia process already mentioned. The tremendously high pressures which he uses permit the employment of a much smaller converter than can be used in the Haber process. The reaction bomb, Fig. 7, is bored out of solid cast alloy steel. It consists of a tube 7 feet long, 9½ inches in external diameter and 4 inches internal diameter. The catalyst tube proper is made of iron and is attached to a plug which closes the pressure tube, being secured by an interrupted thread exactly like the breach mechanism of a heavy gun. A gas-tight joint is obtained by seating the plug upon a copper washer. Sixteen Claude converters capable of synthesizing a total of 20 tons of ammonia per day weigh but 11 tons in contrast to the 70 tons weight of the Haber bomb. The catalyst can be conveniently changed in 10 minutes. The convenience of compact construction also enhances the ease of heat interchange and makes it much easier to maintain the catalyst at a desirable operating temperature.

A typical set-up of apparatus in a Claude unit is shown diagrammatically in Fig. 125. Such extremely high conversions are obtained that it is found economical to use several bombs in series and then permit the unconverted exit hydrogen-nitrogen to return to the process at atmospheric pressure. Thus no high pressure circulating pumps are necessary. Claude recommends four catalyst bombs in addition to a preliminary clean-up bomb in each unit. Two of the bombs in parallel follow the clean-up

bomb, while these in turn are followed by two more bombs in series. The ammonia formed in each converter is removed between bombs. Thus nitrogen and hydrogen after being mixed in a proper ratio pass into a 100 atm. compressor 1, a supercom-
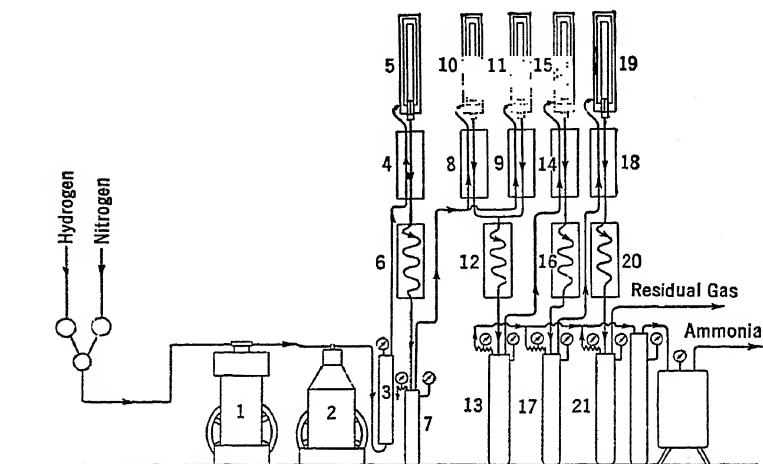


Fig. 125.   The Claude Process.

1—Compressor to 100 atmospheres; 2—Supercompressor to 1000 atmospheres; 3—Scrubbing tower; 4—Heat interchanger; 5—Protector furnace; 6—Condenser; 7—Water collector; 8, 9, 14–18—Heat interchangers; 10, 11–15, 19—Catalyst bombs; 12, 16, 20—Condensers; 13, 17, 21—Ammonia Receivers.

pressor for raising the gas to 1000 atmospheres, 2, a scrubbing tower, 3, for removing traces of oil spray, a heat interchanger 4, preliminary clean-up bomb 5, back through a heat interchanger into a condenser 6.   The water and other condensable materials formed in the clean-up bomb pass into collector 7, and the pure hydrogen-nitrogen mixture passes on through the reacting bombs, heat interchangers, coolers and ammonia collectors as shown.   The passage of the gaseous hydrogen-nitrogen mixture through the two bombs in parallel and two bombs in series converts about 80 per cent of the gases into ammonia.   The remaining unconverted hydrogen-nitrogen gas is expanded back into the hydrogen-nitrogen supply line.

The Claude process, as thus developed, has many advantages. However, the difficulties attending the use of high pressures are also numerous.   Some plants are accordingly known to be compromising by operating at pressures of 500–600 atmo-

spheres, retaining many advantages of the compactness and simplicity of the Claude units without the attending difficulties of super pressure operation.

One difficulty, particularly, is encountered in the super-pressure synthetic ammonia processes such as Claude's, namely, the tendency of the catalyst to overheat at the point at which the gases first come in contact with the catalytic material. The catalyst decreases in activity and, as a result of being overheated, eventually must be replaced. The higher the pressure of operation, the greater this difficulty. Thus, whereas in the Haber processes at 200 atmospheres and with small conversions it is not necessary to change the catalytic material more often than once every 5 or 6 months, in the Claude process a change must be effected every 10 days or so. Casale, in an Italian modification of the original Haber process, claims partially to overcome this difficulty by using a circulating system in which some ammonia is purposely left in the circulating gas at each condensation. Inasmuch as ammonia tends to inhibit the combination of nitrogen and hydrogen, slowing down the rate of reaction, a somewhat larger reaction zone is obtained than would be the case if no ammonia were present in the hydrogen-nitrogen mixture striking the catalyst.

*Cost Considerations.* — The successful operation of a synthetic ammonia process depends fundamentally upon its ability to compete from an economical standpoint with any other possible source of fixed nitrogen. Space does not permit here a complete cost analysis of the synthetic ammonia process, nor an accurate cost comparison between fixed nitrogen obtained by this direct process as compared with that obtained from deposits of nitrates or from other fixation processes. However, it will be interesting to note a few of the cost factors of this catalytic industry and in addition to mention briefly a few of the other commercial processes that have in the past and to some extent do still furnish various amounts of fixed nitrogen annually.

In a cost analysis of a plant for the production of 14,000 tons of ammonium sulfate per year by formation of synthetic ammonia and absorption in sulfuric acid, Ernst [1] has shown that ammonia could be synthesized at a cost of 4 to 6 cents per pound, using electrolytic hydrogen and the above-mentioned "American Process." Of this cost, nearly 75 per cent could be attributed to

[1] Ernst. Am. Inst. Chem. Eng., Dec. (1925).

the cost of producing the pure hydrogen.  This estimate was made in 1925.  Anhydrous ammonia is now being sold on the market for 5 to 6 cents per pound in tank car lots, so that the actual cost has been reduced below the estimates cited above.
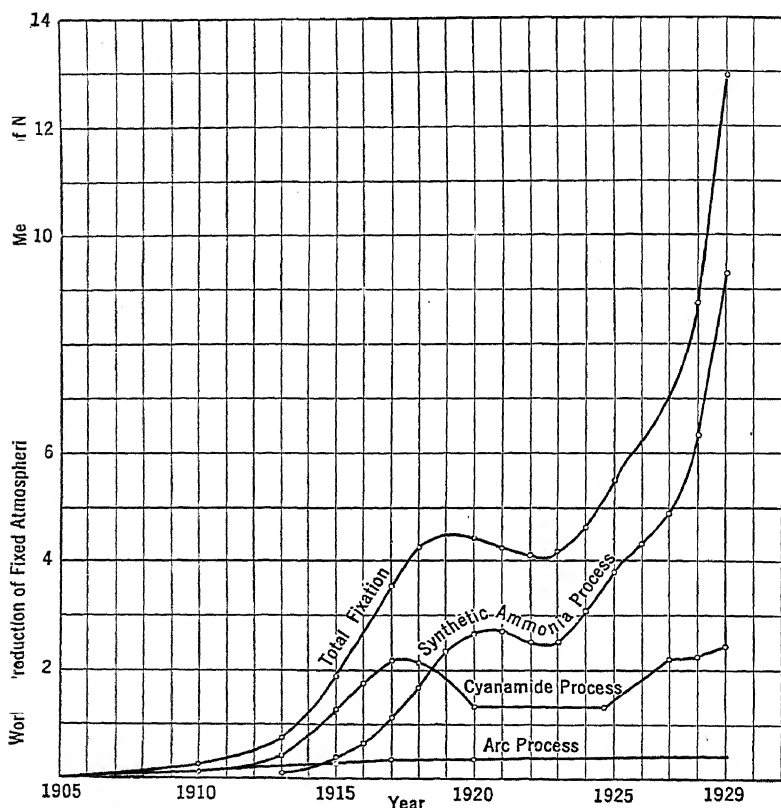


Fig. 126.   Growth and Trend of the Nitrogen Fixation Industry.

*Other Sources of Fixed Nitrogen.* — The production of synthetic ammonia must compete commercially with other sources of fixed nitrogen, including Chilean nitrates, by-product coke oven ammonia, and fixed nitrogen from other fixation processes, as the arc process, the cyanamid process, and the cyanide process. The arc process was formerly used in those countries having an abundant supply of cheap power.  It consists in passing an electric discharge through a stream of air and condensing or

absorbing out the $NO_2$ formed.   The process is rather inefficient and is not keeping pace with the growth of the ammonia industry.   The extent to which the production of synthetic ammonia is rapidly becoming the principle commercial process for fixing atmospheric nitrogen is clearly shown in Fig. 126.   Furthermore, comparison of the production of fixed nitrogen by the arc, cyanamide or synthetic ammonia processes as contrasted with by-product ammonia or Chilean nitrate can be made in Table IV.   The production of fixed nitrogen in the form of synthetic

TABLE IV. — WORLD PRODUCTION OF INORGANIC NITROGEN *
(Short tons of nitrogen per year)

|  | 1909 | 1913 | 1917 | 1924 | 1929 |
|---|---|---|---|---|---|
| By-product ammonia............ | 233,200 | 377,300 | 400,400 | 346,200 | 470,000 |
| Chilean nitrate................. | 330,000 | 429,000 | 431,200 | 372,200 | 539,000 |
| Arc process.................... | 3,300 | 19,800 | 33,000 | 33,000 | 33,000 |
| Cyanamide process............. | 2,750 | 66,000 | 220,000 | 136,400 | 264,000 |
| Direct synthetic ammonia processes....................... | 0 | 7,700 | 121,000 | 275,100 | 1,018,000 |

* From U. S. Department of Agriculture Circular No. 129.

ammonia nearly equalled the entire production of inorganic nitrogen by all other processes, in 1929.

The fixation of nitrogen by the cyanamid process is based upon the reaction:

$$CaC_2 + N_2 = CaCN_2 + C.$$
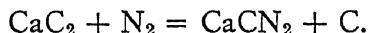
The cyanamide so obtained is used in many fertilizer preparations.   The above reaction is catalyzed materially by various materials including $CaCl_2$, LiCl, NaCl, and $K_2CO_3$.   The catalytic material here seems to function by virtue of its being able to function as a fusible solvent for the calcium carbide.

The production of synthetic ammonia is increasing more rapidly at present than any other method of fixing nitrogen.   About 70 per cent of the nitrogen being fixed by various commercial processes yearly is at present being produced as synthetic ammonia.

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### PROBLEMS ON "CATALYTIC PROCESSES"

51. If the exit flow of gas from a catalyst chamber containing 5 cc. of catalyst is 1251 cc. per minute (S.T.P.) calculate the space velocity being used.

52. A mixture of 3 parts hydrogen and one part nitrogen by volume is passed over 5 cc. of a catalyst at 100 atmospheres pressure and a temperature of 450° C. At 5000 space velocity, 68.3 cc. of ammonia are formed by the catalyst per minute. Bearing in mind the equilibrium percentage ammonia under the above conditions according to Fig. 116, calculate

(a) The per cent ammonia in the exit gas;

(b) What the per cent ammonia in the exit gas would be if the space velocity were dropped to 2500, the entering gas mixture and catalyst volume remaining the same.

53. At 450° C. and 100 atm. total pressure, the per cent $NH_3$ present in a mixture of $NH_3$, $H_2$, and $N_2$ (the $H_2 : N_2$ ratio being 3 : 1) is 16.4 per cent.  Calculate the equilibrium constant,

$$K_p = \frac{(P_{NH_3})^2}{(P_{H_2})^3(P_{N_2})}.$$

Assuming $K_p$ to be independent of pressure, calculate the per cent $NH_3$ that would be present in an equilibrium mixture of 3 : 1 $H_2 : N_2$ and $NH_3$ at 450° C. and a pressure of 1000 atm.  (Compare the result with the experimentally found value recorded in Fig. 2.)

54. Calculate the volume of catalyst that would be needed to permit the passage of 4,000,000 cubic feet of reactants per hour at a space velocity of 25,000.

55. Forty per cent of a 3 : 1 $H_2 : N_2$ mixture passing over an active catalyst at 600 atm. pressure and 450° C. was converted into ammonia.  Calculate the per cent $NH_3$ in the exit gas.  What is the efficiency of the catalyst?  (Catalyst efficiency is usually defined as the fractional conversion of reactants to equilibrium obtained in a single passage over the catalyst.  Thus a .50 efficiency means that the catalyst is producing an amount of ammonia equal to 1/2 of the equilibrium per cent ammonia at the given temperature and pressure.)

56. A gaseous mixture containing 25 per cent $N_2$, 40 per cent $H_2$, and 35 per cent CO is mixed with steam in a ratio of 3 volumes of steam to one volume of gas and passed over a catalyst. Nine-tenths of the CO of the gaseous mixture was converted into $CO_2$ by the reaction:

$$CO + H_2O = CO_2 + H_2.$$
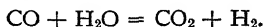
Calculate the (*a*) per cent CO in the exit gas before removal of $CO_2$ or steam, (*b*) per cent CO in the exit gas on a "dry" basis, and (*c*) the per cent CO on a dry and $CO_2$ free basis.

57. If the exit gas from an ammonia converter contains 20 per cent $NH_3$, 60 per cent $H_2$, and 20 per cent $N_2$ and has been passed over a catalyst at a 5000 space velocity based on the volume of exit gas, calculate the number of cc. $H_2$–$N_2$ gas that pass into the bomb per cc. of catalyst per hour.

58. An ammonia converter containing 10 cu. ft. of catalyst is operated at a 20,000 space velocity, a pressure of 600 atm. and a temperature of 450° C. Calculate the yield of ammonia in tons per day obtained if the catalyst efficiency is .5.

# CHAPTER XI

## ABSORPTION OF GASES

ANDREW M. FAIRLIE, D.Eng.

The phrase "absorption of gases" usually means, in chemical engineering practice, the separation of one or more gases from a gas mixture, with a view either to obtaining the separated gas or gases in a form of greater commercial value, or, by purifying the gas mixture from objectionable constituents, to rendering the unabsorbed gas or gases of greater commercial value or applicability. The gaseous components of a gas mixture may also be separated from one another by condensation, sometimes followed by fractional distillation of the condensed liquid; but separation of gases by such means does not fall under the head of "Absorption of Gases."

Gases may be absorbed (*a*) in solids, or (*b*) in liquids. Included under liquids are slurries, consisting of liquids carrying finely divided solids in suspension, such as milk of lime; and solutions, containing dissolved substances. The choice of liquids for absorption purposes is more varied than the choice of solids; but even with liquids, for the absorption of any specific gas, the choice is rather limited, as the liquid chosen must be appropriate for the absorption of the particular gas to be separated from the gas mixture.

### THEORETICAL CONSIDERATIONS

**Distribution Law.** — In any system composed of two or more phases, when a movement of molecules from one phase to another is involved, the equilibrium established is regarded as heterogeneous. The principal influences which affect the equilibria are pressure, temperature and concentration. The principles applying in these cases are the Distribution Law and the Phase Rule. The first statement of the Distribution Law was made by William Henry. Henry's law originally referred only to the equilibrium between a gas and its solution in a liquid, and has been stated thus: the mass of a gas absorbed or dissolved by a given volume of a liquid is proportional to the pressure of the gas

346

at constant temperature. Expressed algebraically, this definition becomes

$$\frac{m}{p} = k,$$

where $m$ is the mass of gas absorbed, $p$ is the gas pressure, and $k$ is a constant. Henry's law, like other gas laws, applies strictly only to ideal gases, and as the gas under observation departs from ideal conditions, the law fails to express the exact relations which exist. Carbon dioxide is an example of a gas that obeys the law of Henry, in the presence of water. On the other hand, the solubility of hydrogen chloride in water is not at all proportional to the pressure. It has been shown experimentally that considerable amounts of hydrogen chloride are soluble in water when the pressure is too low to be measurable. This departure from the law has been ascribed to the dissociation of a solution of hydrogen chloride into electrically charged particles called ions.

**Phase Rule.** — According to the phase rule of Gibbs, the number of conditions (pressure, temperature or composition) which may be varied without causing a change in the number of phases, is equal to the number of components of the system, less the number of phases plus two. This rule is more simply expressed by the equation:

$$F = C - P + 2$$

or

$$F + P = C + 2,$$

in which $F$ signifies the number of conditions that may be varied (degree of freedom); $C$, the number of components; and $P$, the number of phases. For example, in the case of water, a system consisting of a single component, the sum of the degrees of freedom and the number of phases is three. With water above 0° C., two phases, liquid and vapor, exist. The system can therefore yield only one phase that it has not — the solid phase — has therefore only one degree of freedom, or is, in other words, univariant. At 0° C., the presence of three phases (solid, liquid and gaseous) is possible, and thus the system would be nonvariant.

For a more detailed study of the phase rule, the reader is referred to any good book on physical chemistry.

**Absorbent Liquids.** — Liquids are used for the absorption of gases to a far greater extent than are solids. This is attributable partly to the greater choice of liquids available, as compared with solids, and to the greater mobility, and consequent greater ease of handling and regeneration of liquids.

The choice of absorbent liquid for a gas should be determined by careful consideration (1) of the main object aimed at, in separating a gas from a gas mixture, (2) of the nature of the gas to be absorbed, and (3) of the use that is to be made of the product. In the case of scrubbing coke-oven gas with water for the recovery of ammonia, for example, the main object is to remove all the ammonia from the gas mixture, and the concentration of the ammonia liquor produced is of secondary consideration. On the other hand, when brine is to be saturated with ammonia in the ammonia-soda process, the principal purpose of the operation is to obtain as high a concentration as possible of ammonia in the liquid, and a little unabsorbed ammonia in the gas mixture escaping the absorber is relatively unimportant. When it is required to effect a high concentration of an absorbed gas in a liquid, and at the same time to effect complete absorption of the gas, the task is much more formidable than in the other two cases cited. In chemical engineering practice, most cases of absorption of gases by liquids consist of simple solution of the gas in the liquid.

**Absorption Efficiency.** — In a general way, absorption efficiency is dependent on the number of molecules of the gas to be absorbed that come into direct contact with molecules of the liquid absorbent within a given time. The temperature and the velocity of both gas and liquid, as well as the pressure of the gas, all influence the rate of molecular contact of gas with liquid.

The absorption efficiency is also influenced by the total period of contact between liquid and gas, by the solubility of the gas in the absorbent, by the degree of unsaturation and the quantity of the liquid, and, where packed towers are used, by the kind of packing.

**Absorption Equation.** — The problems relating to the absorption of gas by liquid have been studied by Donnan and Irvine.[1]

[1] J. Soc. Chem. Ind., **39**, 23 (1920).

By assuming ($a$) constant and uniform temperature throughout the absorption apparatus; ($b$) a very small percentage by volume of absorbable gases in the gas mixture; ($c$) negligible solubility of the preponderant gases; ($d$) negligible vapor pressure of absorbent liquid; ($e$) uniform flow of gas and liquid; ($f$) wetted area of the walls of the absorption apparatus to be negligible; and ($g$) no complication by relatively slow side reactions, these authors developed a number of equations relating to absorption. A specific example of equations of this sort is that deduced by Partington and Parker,[2] for absorption towers designed for nitrous gases, $viz.$:

$$\log_e \frac{C_0}{C} = \frac{KkA}{V} \cdot x,$$

In which

$C_0$ = initial concentration of entering gas in pounds $NO_2$ per cubic foot,

$C$ = its concentration at a height $x$ in the tower in the tower in pounds $NO_2$ per cubic foot,

$A$ = cross section of the tower in square feet,

$V$ = rate of gas flow in cubic feet per minute,

$k$ = area of packing surface exposed in square feet per cubic foot of gross volume occupied by packing,

$K$ = a coefficient (not constant) depending on the rate of absorption of $NO_2$ in various concentrations of nitric acid calculated from the results of Rideal.[3]

In computing the above equation, such factors as changes in volume of gas or in concentration of nitric acid absorbent, and the rate of solution of nitric oxide in nitric acid were not considered. If it be granted that these features are negligible, the equation will give approximate results for the size of towers necessary for the absorption of a stated amount of $NO_2$ from gas of known concentration, using an absorbent liquid containing a given amount of nitric acid. It is obvious that this equation is quite narrowly limited in its application, and the difficulties of computing an equation which would be exact or of wide application must also be apparent.

[2] J. Soc. Chem. Ind., **38**, 75 T (1919).
[3] J. Ind. Eng. Chem., Dec. 1920.

**Mechanism of Gas Absorption.** — The mechanism of the absorption of gases by liquids can be visualized by the method of Lewis and Whitman.[4] The liquid film and the gas film at the point of contact are imagined as having a definite thickness. Beyond the gas film, conditions in the gas are the same as in the main body of gas; and beyond the liquid film, conditions are the same as in the main body of the liquid. But at the point of contact the gas and the liquid are in equilibrium. Absorption occurs by penetration of the two films consecutively. The rate of absorption per unit of surface area equals the diffusion coefficient for the gas film multiplied by the difference in partial pressure across the gas film, and also equals the diffusion coefficient for the liquid film multiplied by the difference in concentration across the liquid film. With water or very dilute solutions, the rate of absorption is determined solely by the rate of diffusion through the gas film, so that the gas is absorbed rapidly. With liquids of high concentration, on the other hand, the absorption of a small amount of gas by the liquid film brings the liquid surface into equilibrium with the gas, thereby preventing further absorption until the absorbed gas has diffused from the liquid film into the body of liquid beyond the film.

**Absorption Apparatus.** — After a study of absorption rates of gases in agitated liquids and in quiescent liquids, Monaweck and Baker[5] reached the conclusion that practical absorption apparatus which constantly creates new contacts between gaseous and liquid phases, thus reducing the chances for the formation of films of gas and of liquid, are especially effective, and give much higher overall coefficients of absorption than apparatus that favors the development of gas and liquid films.

Those desiring to pursue further the study of the theories relating to absorption are referred to a series of papers presented in an "Absorption Symposium" before the Division of Industrial and Engineering Chemistry at the 68th meeting of the American Chemical Society, Ithaca, N. Y., Sept. 8–13, 1924, and published in Industrial and Engineering Chemistry, 16, 1215–1242 (Dec. 1924).

[4] Chem. and Met. Eng., 29, 146 (1923); Ind. Eng. Chem., 16, 1215 (1924).
[5] Trans. Am. Inst. Chem. Eng., 22, 165–183 (1929).

## MEANS FOR EFFECTING THE ABSORPTION OF GASES

**Absorption by Means of Solids.** — Examples of solids used for the absorption of gases are calcium chloride (for water vapor); caustic soda (for water vapor or carbon dioxide); phosphorus (for oxygen); hydrated lime (for chlorine, in the manufacture of bleaching powder); and activated carbon and silica gel (for the absorption of various gases). Activated carbon, which is an adsorbent rather than an absorbent, is made from the shells of certain nuts and the seeds or pits of certain fruits, or from coals or low temperature cokes, which are charred at a low temperature (below 600°–700° C.) in such a way as to yield a dense carbon containing a minimum of adsorbed hydrocarbons. The carbon deposited will be inactive in proportion to the amount of hydrocarbons adsorbed within the pores. The adsorbed hydrocarbons may be removed by certain solvents, by prolonged calcination, or by selective oxidation, to increase the activity of the carbon.

*Activated carbon* contains within its structure sub-microscopic capillaries which, from vapor pressure measurements, have been calculated to be of the order of $10^{-6}$ cm. in diameter. The surface available per cubic centimeter of highly activated cocoanut carbon has been variously computed at from 120 to 1000 square meters. When such carbon is exposed to a high or low concentration of condensible vapor, a considerable amount is adsorbed on the immense surface of the capillaries.

Activated carbon has been used efficaciously in gas masks, to protect the wearer from injurious or poisonous gases. It is used also to some extent to remove objectionable odors from gases discharged from industrial works, and to purify air admitted into buildings. Industrially, it has been used to extract gasoline from natural gas, for recovering solvents, etc. The dense activated carbons for the adsorbtion of gases should be distinguished from the porous activated carbon used for decolorizing liquids. Used activated carbon can be regenerated for further use by careful heating to 600°–700° C.

*Silica gel* is produced by treating a solution of silicate of soda (waterglass) with sulfuric acid, and by thoroughly drying the resultant jelly-like mass. The product, chemically, is silicon dioxide. The process of drying the gel develops throughout its internal structure myriads of pores of infinitesimal size. So minute are these pores, that no matter how finely the dried gel

may be pulverized, each particle retains the physical structure and properties of the larger masses. After drying, the gel is crushed or pulverized, and activated by heating to a high temperature. It is marketed in various sizes, from 1/4-inch mesh to the fineness of an impalpable powder, depending on the use to which it is to be applied.

*Activated silica gel* is both an absorbent and an adsorbent. As an absorbent it can make a selective separation, or absorption, of a gas from a gas mixture. As an adsorbent it can condense certain gases to the liquid phase within its pores. As an absorbent of gases it has been tried in various industrial fields, but has not attained a wide application. As an auxiliary in refrigeration apparatus, it serves both as absorbent and adsorbent. In this capacity, the activated gel absorbs sulfur dioxide gas from above the surface of a body of the liquid gas contained in a tank or coil, causing more of the liquid gas to evaporate, thus producing the refrigerating effect. The silica gel, when saturated with gas, is regenerated by a gas flame, controlled automatically by a thermostatic device. The absorbed gas is driven out of the gel, is conveyed through pipes to a condenser where it is again liquefied, and the liquid flows back to the refrigerating tank or coil.

**Absorption by Means of Liquids.** — There are three methods in common use for contacting gas with liquid, *viz.:*

1. Passing the gas in small bubbles through the liquid.

2. Passing the finely divided liquid, as a spray or mist, through the gas.

3. Passing the gas through the interstices of an enclosed space packed with solids having extensive superficial area over which the liquid is caused to flow.

*Bubbler Tower.* — The most common type of bubbler absorber is the tower shown in Fig. 127. This tower is composed of cylindrical tower sections, each about 3.5 feet high and from 3 to 6 feet in diameter, fitted one on top of another, with the joints suitably sealed. Each section has at the bottom a flat plate with a large hole in the center, and above each plate there is a perforated bell. The gas enters the tower under pressure through the pipe *C*, and passes in counter-current to the descending liquid as minute bubbles passing through the perforations in the bells.

The bubbler tower brings the finely divided gas under pressure

into intimate contact with the liquid, and is an efficient form of absorber. Its chief objection lies in the expense for power necessary to force the gas through a sufficient depth of liquid.

*Unpacked Tower.*—To pass a mist or spray of liquid through the gas is to use an unpacked (v o i d) tower, or its equivalent. The following have been advanced as disadvantages of the void tower:

1. To avoid collection of a considerable part of the sprayed liquid on the tower walls, the tower must be of large diameter.

2. Without packing, mixing of t h e g a s e s within the tower is lacking.

3. In t o w e r s high enough to afford the necessary period for contact of gas with liquid, there would be a tendency for the fine particles of liquid to coalesce into large drops.



FIG. 127. Bubbling Absorption Tower; Used for the Absorption of Carbon Dioxide in the Ammonia Soda Process.

4. The cost of providing the necessary surface area for contact of gas with liquid is greater for the necessary period of time than with packed towers.

On the other hand, the void tower requires the minimum of power for the movement of the gases, and the expense of the tower packing is saved. In practice, the void tower has not come into general use. Experiments with it are continually in progress, however, and as the advantages it offers are quite attractive, means for making it an efficient absorption device may yet be developed.

*Design of Packed Tower.* — The packed tower is the standard apparatus used in many industries for the absorption of gases in

liquids.  Consequently, the shape and size of the tower, and the quality and characteristics of the kind of packing used, are of the greatest importance.

An absorption tower should, of course, be built of materials that are durable and capable of withstanding for many years the action of the chemicals (gaseous and liquid) to be handled, at those temperatures that will prevail.  It should be stably built on secure foundations, and the walls should be able to support any side-thrust that may be exerted by the packing.  The gas-inlet flue should slope downwardly towards the tower, and its junction with the tower should be high enough above the liquid outlet to prevent the entrance of liquid from the tower pan into this flue.  The gas-outlet flue may be on the side of the tower near the top, or it may come out of the top itself, vertically. The latter design eliminates any possibility of the splashing of liquid into the gas-outlet flue.

*Shape and Size of Absorption Towers.* — Opinions vary as to the preferred shape and size of absorption towers.  Obviously the size should vary with the kind of gas to be absorbed, with its concentration in the gas mixture, and with the volume of gases and liquids to be handled per unit of time.  Circular towers are frequently preferred to square towers, on the grounds that it is difficult to distribute liquid or gas properly into the corners of a square tower, and that the circular tower is a more stable structure.  On the other hand, the square tower can be built of bricks of standard size and shape, whereas the circular tower requires special radial brick; and the square tower utilizes more efficiently the ground area allotted for the structure.  Small towers, up to five feet in diameter, are usually circular, as they can be built of cylindrical stoneware tower sections of standard size (Fig. 128). Occasionally towers are built of octagonal or rectangular cross-section.

It has been claimed that the diameter of an efficient absorption tower should not exceed ten or twelve feet, and that the height should be not less than five or six times the diameter.

It is generally conceded that a tall narrow tower is likely to absorb more efficiently than one that is wide and short.  The factors of resistance to gas-flow and of initial cost must be considered, however.  Many modern large-scale operations could not be accommodated in a tower of a diameter of but twelve feet, hence it has been found practicable to build and to operate
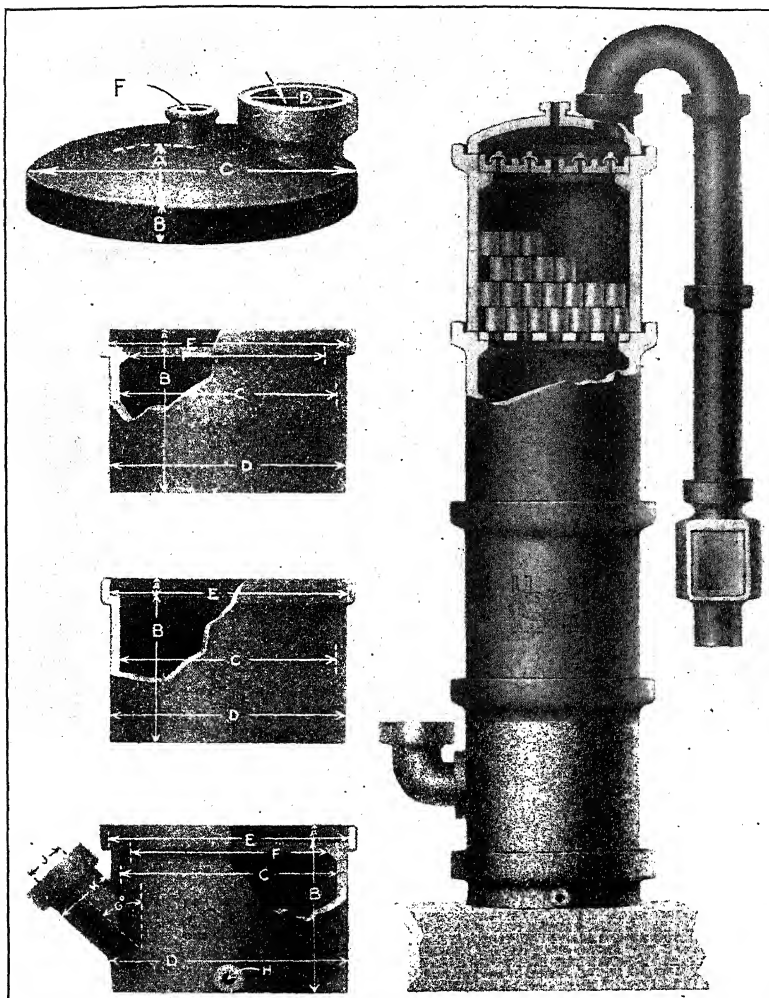
FIG. 128. Stoneware Tower Sections and Complete Tower.

Tower Top

Liquid Seal
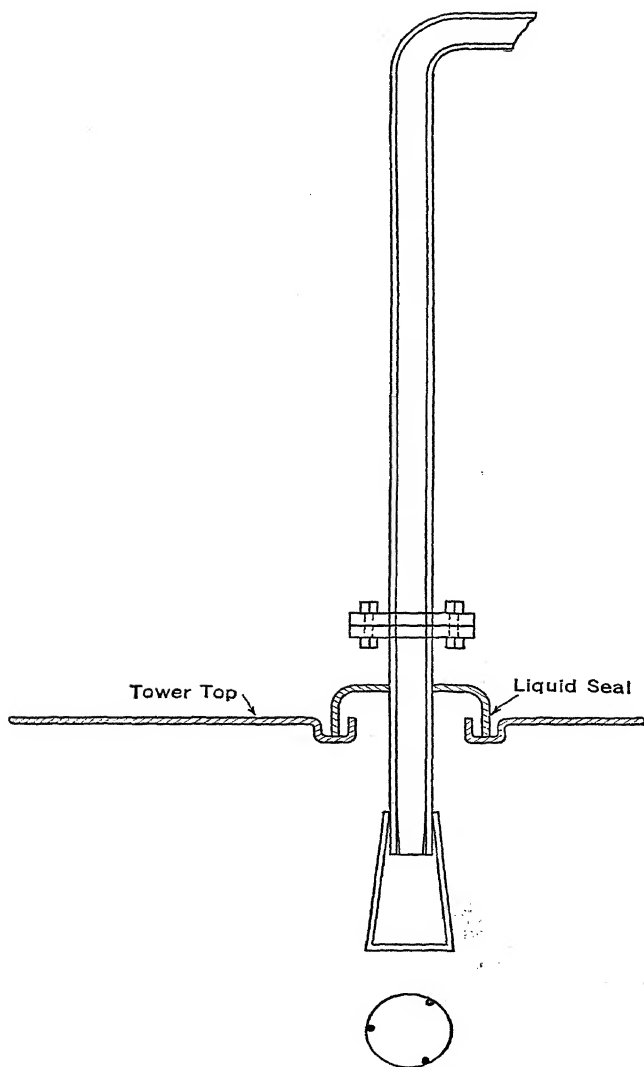
FIG. 129. Liquid Distribution Splash-plate Type of Large Towers.

absorption towers as much as thirty feet in diameter. With wide towers, careful attention must be given to the design of gas-inlet flues and of spaces between the supporting piers for the packing, in order to facilitate the distribution of the gas at the bottom of the tower. The proper distribution of the liquid at the top of a wide tower must also be provided for. A convenient type of distributor for a large tower is shown in Fig. 129. The height of a tower is usually limited to 70 or 80 feet, on account of the difficulty of pumping liquid to a higher elevation with a single-stage pump. The remedy for the short period of contact between liquid and gas, in a wide tower whose height is only two or three times its diameter, is to employ two or more of such towers, in series. It is economical, however, to construct the absorption space in a few units rather than in many, inasmuch as, in each unit, the unpacked spaces at the bottom and top, beneath and above the packing, are of little absorptive value; furthermore, each unit must have its top and its bottom, its inlet- and its outlet-flues, and all the accessories. These features, together with the non-productive unpacked spaces may cost from one-fifth to two-fifths of the cost of a complete tower. The advantage of avoiding a multiplicity of units, where the same packed volume can be satisfactorily encompassed in a few units, is, therefore, obvious.

*Accessories of Absorption Tower.* — An absorption tower of relatively large size is shown in vertical section in Fig. 130. The usual accessories of an absorption tower are a receiving tank at the bottom for the discharged liquid, another at the top for the feed liquid, a distributing apparatus for distributing the liquid over the surface of the tower packing, a pump for elevating the feed liquid, and a blower or fan for moving the gases through the tower. In some cases, where the discharged liquid is recirculated, either over the same tower or over another tower in a series, the liquid is passed through a cooler before being re-pumped.

*Tower Packing.* — The importance of selecting the right kind of packing for an absorption tower has been referred to above. In making the choice, the principal features to be considered are:

1. Durability in the presence of the particular gases and liquids to be handled.

2. Effective (or wetted) surface area, per cubic foot of packed tower space.

3. Free space, or interstitial space, per cubic foot of packed tower space.

4. Freedom from channeling or pocketing of liquids, as packed in a tower.

5. Resistance to gas-flow
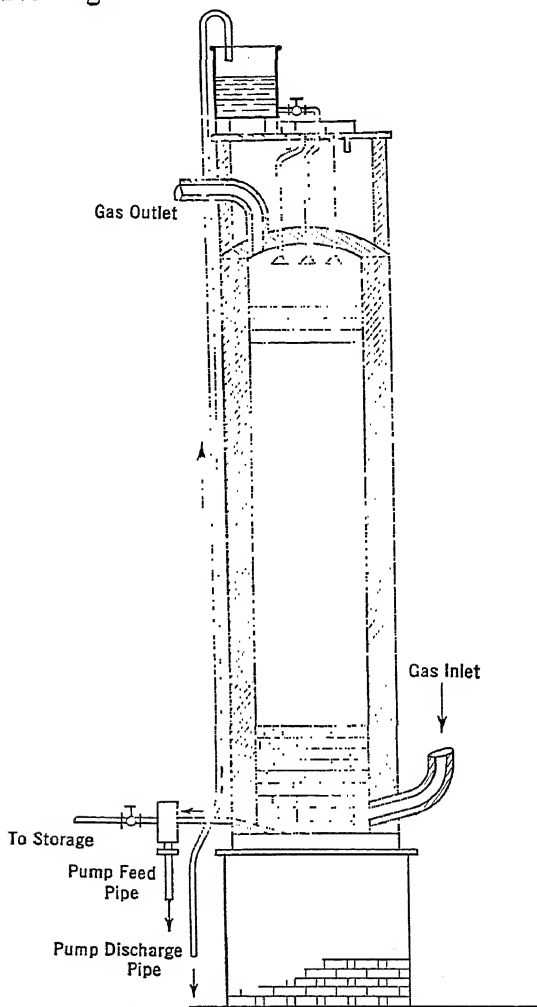


Fig. 130.    Large Scale Absorption Tower.

6. Freedom from tendency to accumulate deposits of finely divided solids carried by the gases or liquids.

7. Weight per cubic foot of packed space.

8. Stability of position, as packed, and freedom from exertion of lateral pressure.

9. Period of contact between liquid and gas, while passing through the packing.

10. Cost in place in the tower per square foot of effective surface area.

*Types of Packing Units.* — For many years the materials used for packing absorption towers were chiefly lumps of broken quartz, or of coke, arranged in the tower in graduated sizes, the largest at the bottom. Brick checkerwork, also, has been used extensively, and is still in use in many towers. Manufactured forms of packing, in modern practice, have been largely replacing quartz, coke and brick checkerwork, and a wide variety of tower "packers" are now available to the engineer. The manufactured packers were designed to afford greater surface area, greater interstitial space, etc., than was possible with large solid bodies such as bricks or lumps of quartz and coke. Of the ten different features enumerated above, as the points to be considered in choosing a type of tower-packing, some manufactured forms excel in one respect, others in a different one. Some comparative tests have been made, to determine the relative desirability of the different forms for different purposes, and some of the results obtained have been published. The resistance to gas-flow, the effective surface area and the interstitial space of several shapes of manufactured packers, as compared with lumps of quartz and coke, have been studied experimentally by Zeisberg.[6] For complete details the reader must refer to the original article. The following brief abstract of results is all that can be reproduced here:

1. The frictional resistance of any packing is proportional to the square of the velocity of gas-flow.

2. Resistance to gas-flow increases rapidly with decrease in the size of the packer units.

3. With small sizes of packer units, the resistance of wet packing is much greater than with dry packing.

4. With nearly all kinds of packers, the resistance either dry or wet is less than the resistance with liquid circulating through the packing.

5. For any given size of packing, the manufactured forms afford much more surface and greater interstitial space and inter-

[6] Trans. Am. Inst. Chem. Eng., 12, Part 2, 231 (1919).

pose much less resistance, than quartz or coke. An example is given showing that the resistance offered by 3-inch coke is more than twice as much as for 3-inch spiral rings.
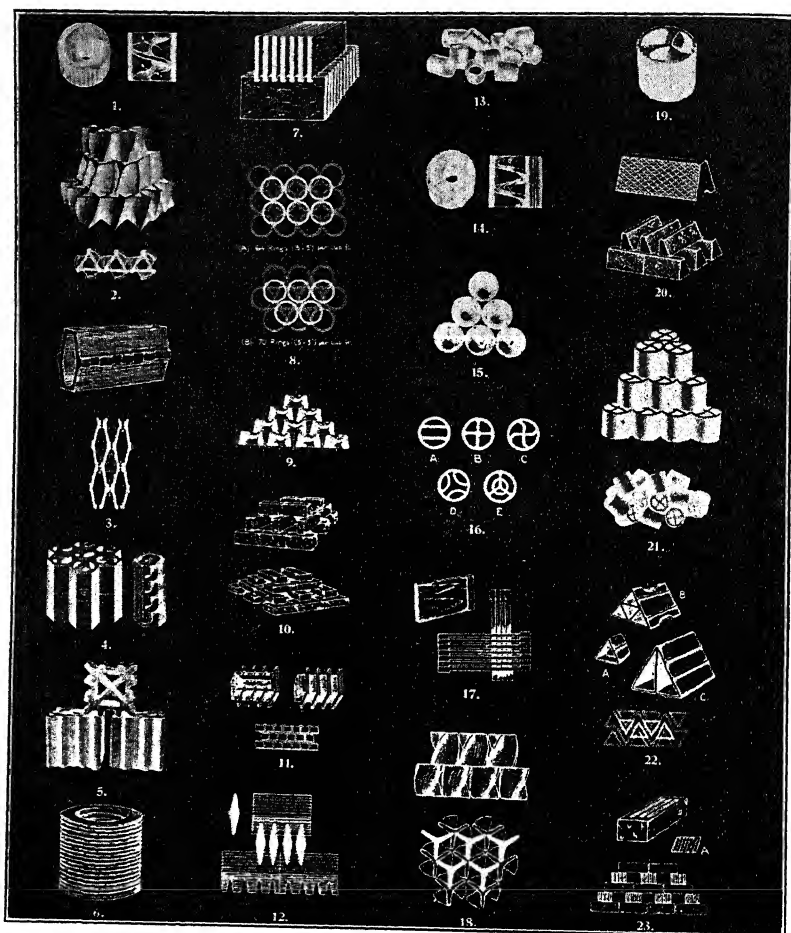


Fig. 131. Types of Absorption Tower Packing Units, and Methods of Packing.

A table of coefficients pertaining to several types of packing units is given, also a method of using the coefficients for the calculation of the pressure necessary to force gas through an absorption system of known dimensions and packed with a given depth of certain forms of packers.

TABLE I. — PACKING UNITS

| (1) No. in Fig. 5 | (2) Name* | (3) Size of Unit | (4) Number of Units per Cu. Ft. | (5) Sq. Ft. Surface per Cu. Ft. Packed Tower Space | (6) Free Space (Per Cent of Total Packed Tower Space) | (7) Sq. Ft. Surface per Cu. Ft. of Free Space | (8) Weight (as Packed) Lbs. per Cu. Ft. |
|---|---|---|---|---|---|---|---|
| 1 | Chemico spiral rings | 6"×6" | 8 | 15 | 58 | 26 | 53 |
| 1 | Chemico spiral rings | 3"×3" | 64 | 29 | 64 | 44 | 53 |
| 2 | Nielson propellor "B" | 6"×6" | 12 | 17.5 | 80 | 22 | 34 |
| 3 | Guttman cells | 9"×6"×3" | 10⅔ | 22.5 | 74 | 30 | 45 |
| 4 | Hexahelix | 4"×4" | 28 | 20 | 60 | 33 | 60 |
| 5 | Hechenbleikner blocks | 6"×6"×6" | 8 | 14.3 | 62 | 23 | 52 |
| 6 | "Nori" ribbed rings | 4.5"×4" | 24 | 23 | 65 | 35 | 80 |
| 7 | Tile packing "A" | 10"×5"×1½" | 19 | 13.7 | 73 | 19 | 48 |
| 8 | Plain rings | 4.5"×4" | 24 | 20 | 51 | 39 | .... |
| 9 | Cone packing | 6"×3" | 18 | 8 | 60 | 13 | 39 |
| 10 | Brick checkerwork "A" | 9"×4½"×2½" | 9½ | 6.7 | 45 | 15 | 81 |
| 11 | Obsidianite packers | 9"×4½"×3" | 14¼ | 18 | 59 | 30 | 64 |
| 12 | Scherfenberg bricks | 9⅝"×7"×3⅝" | 8 | 10.6 | 44 | 24 | 60 |
| 13 | Raschig rings, dumped in | 2"×2" | 170 | 33.5 | 83 | 40 | 32 |
| 14 | H. H. spiral rings | 3⅛"×3⅛" | 60 | 30 | 50 | 60 | 55 |
| 15 | Hollow balls | 2½" | 140 | 19 | 33 | 58 | 52 |
| 16 | Straight partition rings "B" | 4"×4" | 27 | 25 | 50 | 50 | 70 |
| 17 | Wheatly cells | 10"×6½"×½" | 32 | 26 | 40 | 65 | 70 |
| 18 | Nielson propellor "A" | 6"×6" | 13 | 16 | 77½ | 21 | 40 |
| 19 | Triple spiral rings | 3¼"×3¼" | 55 | 37 | 60 | 62 | 55 |
| 20 | Prismic packing | 12"×4½" | 7 | 5.5 | 30 | 18 | 55 |
| 21 | Partition rings, dumped in | 3"×3" | 45 | 24 | 63 | 40 | 42 |
| 22 | Prym triangles | 3¼"×3¼" | 55 | 40 | 72 | 55 | 60 |
| 23 | Brick checkerwork "B" | 9"×4.5"×3" | 10⅔ | 15.4 | 40 | 39 | 96 |
|  | Coke lumps | 6" |  | 5.5 | 57 | 10 | 26 |
|  | Coke lumps | 3" |  | 12 | 50 | 24 | 30 |
|  | Quartz lumps | 6" |  | 6.3 | 48 | 13 | 87 |
|  | Quartz lumps | 3" |  | 13.7 | 43 | 32 | 92 |

* Manufactured forms are computed on a "packed in" basis, except where "dumped in" is specified.

The characteristics of a great many manufactured forms of packers have been tabulated and charted by Butcher.[7]

Figure 131, reproduced from the article cited, illustrates the different shapes studied.   Table I serves as a key to the figure, and also quotes numerical data pertaining to the various shapes, from a tabulation prepared by Butcher.

*Characteristics of Packer Units.* — It will be noted that the various types of packers differ among one another in the advantages and disadvantages that they possess.   A packer that has very high free space is apt to be deficient in surface area, or one that is high in both free space and surface area is likely to offer high resistance to gas-flow.   In general, the smaller the units, the greater the surface area, and also the greater the resistance. Excessively high free space may involve deficiency of surface area, just as excessive surface area may connote fragility or liability to collect deposits of sediments, or to induce channeling. Excessively low resistance to gas-flow may indicate that the gas escapes contact with a large part of the surface of the packing, or that the period of contact between liquid and gas is too brief. Before choosing a packer, therefore, all the characteristics of each type under consideration should be weighed, in their relation to the requirements of the problem in hand.

Manufactured forms of packing are usually made of hard-burned ceramic material, to render them thoroughly resistant to acids as well as to other chemicals.   The above table brings out quite clearly the superiority of nearly all types of manufactured packing to quartz, as regards weight per cubic foot, and to both coke and quartz, as regards surface area.   Another advantage of most of the manufactured forms, over both coke and quartz, is the comparative freedom from side-thrust against the walls of the tower.   Unless the units are dumped into the tower at random, the manufactured designs are more or less self-supporting.

*Arrangement of Packer Units.* — The manufactured packers may be placed in the tower in a variety of ways.   In some cases, as suggested above, they are dumped at random, although this is not a preferred method, except, perhaps, where the small Raschig rings are used.   Usually the packers are arranged in layers, and here there is the option between laying each unit exactly superposed on its counterpart beneath, with axes of adjacent vertically disposed units coinciding, or of "staggering"

[7] The Industrial Chemist and Chemical Manufacturer, 446 (Nov. 1928).

the units of adjacent courses, so that any one unit rests on parts of three units beneath, or on parts of four units beneath, according to the method of staggering adopted. Many of the packers, such as the Nielson propellors and the various spiral cylinders or "rings," are designed to be packed in staggered courses. The Hexahelix units, on the other hand, are designed to be fitted against one another snugly, and to be superposed one on top of another exactly, so that no straight-flow or random passages are provided, for either gas or liquid.

### The Absorption of Gases in Technical Practice

A few examples will be cited to illustrate the practical application to industry of the principles and types of apparatus outlined above.

**Absorption in the Ammonia-Soda Process.** — The Solvay process for the production of carbonate of soda (soda ash) furnishes an excellent example of the absorption of a gas under pressure. A strong solution of common salt (brine) is saturated with ammonia gas in a tank having a perforated bottom, beneath which the ammonia is introduced. The ammoniacal brine is then pumped to a tower (Fig. 127) called the carbonating tower, from 50 to 65 feet high, made of cast-iron rings or tower sections about 6 feet in diameter and 3.5 feet high each. The ammoniacal brine is forced into the tower, a little above the middle of its height, through the pipe $P$. The carbon dioxide, introduced as a gas mixture containing about 30 per cent $CO_2$, enters the base of the tower under pressure through pipe $C$, and, rising in small bubbles through the perforations of the numerous domes or bells in the tower, comes into intimate contact with the ammoniacal brine by which it is absorbed, with the production of bicarbonate of soda and ammonium chloride, according to the equation:

$$NaCl + NH_3 + H_2O + CO_2 \rightarrow NaHCO_3 + NH_4Cl.$$

The bicarbonate of soda is precipitated, and is washed down the tower by the descending liquid, which escapes, thick and milky, from the outlet at the bottom of the tower. A low temperature (not below 35° C.) is desirable. The holes in the bells gradually become clogged with crystals of bicarbonate of soda, and every ten days or so the tower must be drained, and the crystals dissolved with hot water or steam. The usual practice is to

employ several towers, so that one may be taken out of service at intervals for cleaning, without interrupting the process.

The residual gases discharged from the top of the carbonating tower, consisting chiefly of nitrogen, with some ammonia and carbon dioxide, pass through pipes to scrubbers, in which they are treated with brine and dilute sulfuric acid to recover the residual ammonia. The unabsorbed carbon dioxide is allowed to escape.

**Absorption in the Manufacture of Hydrochloric Acid.** — Hydrochloric acid gas is readily absorbed by water with the evolution of heat, as follows:

Mols water per mol HCl. .1    2      5      10     50     100     200
Calories. . . . . . . . . . . . . .5.375   11.365   14.959   16.157   17.115   17.235   17.315

When a concentration of 20.24 per cent by weight of HCl is reached the character of the solution changes. At and below this concentration the acid is probably held as a hydrate. The vapor tension of the water in such relatively dilute solutions is high, and very little acid is vaporized from them on boiling, or can be blown out with air.

Acid of a higher concentration than 20.24 per cent has a high vapor tension of HCl which increases rapidly with increases in temperature and concentration. The acid in excess of 20.24 per cent can be readily removed by distillation or by blowing air through the solution. Hydrochloric acid of high concentration can therefore be produced only by carrying out the absorption at low temperatures or by maintaining a high concentration of HCl vapor in contact with the acid solution. Table II, calculated by Laury,[8] gives the relation between temperature, gas concentration and strength of the acid solution:

TABLE II. — MINIMUM GAS CONCENTRATIONS REQUIRED TO MAKE 18°, 20° AND 22° BÉ. HYDROCHLORIC ACID

| Temp. °C. | 18° Bé. Per Cent HCl by Vol. | 20° Bé. Per Cent HCl by Vol. | 22° Bé. Per Cent HCl by Vol. |
|---|---|---|---|
| 0 | 0.098 | 0.46 | 2.24 |
| 10 | 0.23 | 1.51 | 4.41 |
| 20 | 0.47 | 1.94 | 8.23 |
| 30 | 0.94 | 3.69 | 14.46 |
| 40 | 1.85 | 6.80 | 25.59 |

[8] N. A. Laury: "Hydrochloric Acid and Sodium Sulfate," 1927, p. 98. Chemical Catalog Co., Inc.

*Concentration of the Gas.* — Commercially hydrochloric acid is always produced by the absorption of HCl gas, formed by various methods, in water. The initial concentration of the gas, as is evident from Table II, will have an important influence on the method of absorption to be adopted. As the HCl is absorbed, the concentration of the gas will decrease so that it will be necessary to provide for the absorption of weak gases. This is usually provided for by counter-current flow of gas and liquid. The fresh water thus comes into contact with a gas mixture that is almost free from hydrogen chloride, while the most concentrated gas encounters acid that is already strong in the hydrates of hydrochloric acid. The temperature is controlled by cooling the gases before absorption and also the acid during the absorption process.

The reaction between common salt and sulfuric acid producing salt cake and hydrochloric acid is the most common source of the acid. The thermal reactions are represented as follows:

$$NaCl + H_2SO_4 \rightarrow HCl + NaHSO_4 + 0.8 \text{ cal}$$

$$NaCl + NaHSO_4 \rightarrow HCl + Na_2SO_4 + 15.0 \text{ cal.}$$
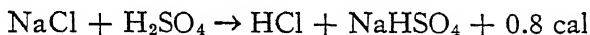
The reactions are only slightly exothermic, and therefore, to carry them to completion rapidly, extraneous heat must be applied. The decomposition takes place in furnaces of various types, fired with coal or other fuel. Of the two products of the furnacing operation, the one that is of interest here is the hydrogen chloride.

*Cooling the Gas.* — The gas evolved from a pot-and-muffle furnace may vary in its percentage of HCl from 5 to 30 per cent. The gas, as evolved, is hot and must therefore be cooled before going to the absorbers. A satisfactory cooling apparatus is the S-bend cooler, made of fused silica pipes 6 inches in diameter, sprinkled with flowing water (Fig. 132). Since the gas mixture contains moisture, some condensation of hydrochloric acid solution takes place in the cooler. Ordinarily the gas mixture from a pot-and-muffle furnace is pure anough to be admitted from the cooler directly into the absorbers, but in some cases a coke filter for the removal of impurities is advisable. Beyond the gas cooler, chemical stoneware of the best grade is used for conveying the gases.

*Absorption Equipment.* — The absorption of hydrochloric acid gas was formerly effected in Woulff tourills or in water-cooled absorbers of the Cellarius or the Meyer type.[9]    The type of
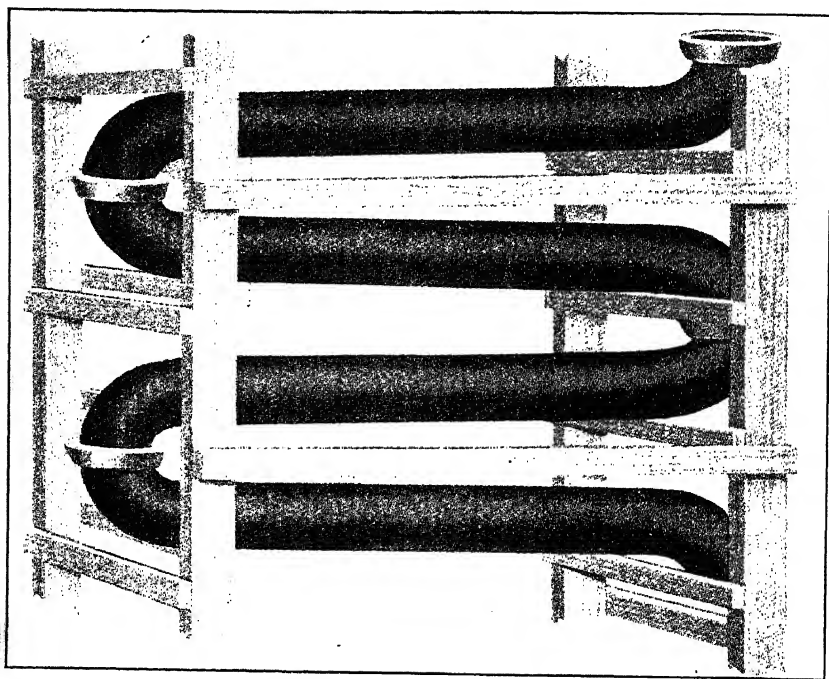


FIG. 132.    S-bend Gas-Cooler.

absorber recommended by Laury as having the highest capacity per unit area and volume, and as being the cheapest and most durable is the packed tower.    Figure 133 (reproduced from Laury) shows a typical hydrochloric acid absorption equipment for concentrated gases.    The direction of gas flow is indicated by arrows. The two towers, of chemical stoneware, 40 inches in diameter and containing 12 vertical feet of egg-sized coke packing, are adequate, according to Laury, to absorb all of the hydrogen chloride from 300 cu. ft. of gas per minute containing approximately 30 per cent of HCl.    The rear tower, or scrubber, is fed with water, evenly distributed over the top of the packing, at such a rate as to produce

[9] See Laury, *op. cit.*, 103 ff.

a discharge liquid of about 13° Bé. in strength. A portion of this discharge acid may be recirculated over the scrubber to advantage, but if so, sufficient water must be added to keep the concentration of the discharge from this second tower below 13° Bé. The surplus liquid discharged from the rear tower is fed to the front tower, which receives the gas from the filter. The front tower is provided with a cooler for the circulating liquid. The gas velocity in these towers is about one linear foot per second,
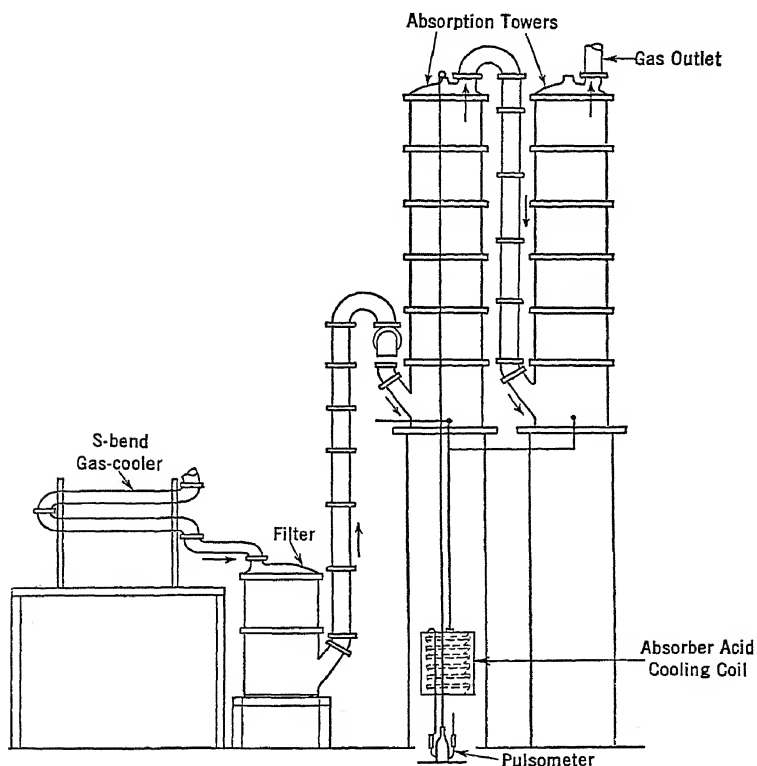


FIG. 133. Hydrochloric Acid Absorption Apparatus for Concentrated Gases.

and is maintained by a stoneware, duriron or rubber-lined fan. The resistance to gas-flow of each of these towers, coke-packed, is from 1/8 to 3/8 of an inch of water.

*Vitreosil Absorber.* — On account of the low heat conductivity of the walls of a packed stoneware tower, the removal of the heat

generated is difficult. This is not a serious objection if a low concentration of acid is being produced or if the initial concentration of the gas is high. A recently devised apparatus which is an improvement on the older types of absorbers is the water-cooled Vitreosil absorber which is of the S-bend type with a wide body and a weir adjacent to the spigot outlet to cause a reservoir of absorbent in each piece. This absorber is free from most of the objections to the older types in that the gas and liquid travel through the same outlet and all joints are above the liquid level. Because of its design the units are set up vertically, exactly like the cooler sections in Fig. 132, and thus are economical of floor space. The walls are much thinner than is usual for fused silica ware and hence the water cooling is very efficient.

**Absorption in Sulfuric Acid Contact Processes.** — In contact processes for the manufacture of sulfuric acid, a catalyst serves to effect the oxidation of $SO_2$ to $SO_3$, in a gas mixture containing originally from 7 to 10 per cent of sulfur dioxide. After passing the catalyst, the gas mixture goes to a heat exchanger, then to a gas cooler, and finally to the absorbers. The latter are usually cylindrical towers of iron or steel, lined with acid-resistant brick laid in silica cement (powdered quartz mixed with silicate of soda solution). These towers are about six or eight feet in internal diameter, and from 25 to 40 feet high. They are packed, nowadays, with manufactured packers, and are usually connected two or more in series. The absorbing liquid is sulfuric acid, cooled to from 50–100° C. For the most efficient absorption a concentration of from 98.5 to 99 per cent $H_2SO_4$ must be maintained. The reason for the high absorption efficiency of the concentration specified is that sulfuric acid of this strength possesses the minimum vapor pressure.

*Concentration of the Absorbing Acid.* — In each absorber, the gas and liquid usually flow counter-current to each other. In a series of absorbers, the absorbing acid is recirculated over and over again, on each unit, and, owing to the absorption of $SO_3$, the volume of the liquid constantly increases. The surplus flows to the next forward tower in the series, and the surplus from the first tower flows to storage for shipment. Likewise, owing to the constant absorption of $SO_3$, the concentration of the acid circulating over each tower tends to increase continuously. No particular attention is paid to this increase in concentration

on the forward towers of a series, but on the last tower, which affords the last chance to complete the absorption of $SO_3$ before discharging the gases to atmosphere, the maintenance of a concentration of between 98.5 and 99 per cent $H_2SO_4$ in the supply acid must be attended to with scrupulous care. The acid circulating in the last tower is therefore continuously diluted, either with water or with dilute sulfuric acid, to maintain the desired concentration. Since the increase in concentration in the final tower is not uniform enough to permit the introduction of a uniform quantity of water or dilute acid continuously, without observation or adjustment, it is necessary to keep watch on the concentration of the discharge acid of this final tower, in order intelligently to control the rate of dilution. Fortunately the electrical conductivity of concentrated sulfuric acid varies quite widely within the range 95–99.5 per cent $H_2SO_4$ for very small variations in concentration, and an adaptation of the Wheatstone bridge has been devised to serve as an instantaneous indication of the concentration of this acid. Most contact plants are now equipped with a modification of this device in which a telephone receiver has been substituted for the galvanometer. By means of this equipment it is literally possible to *listen* to the strength of sulfuric acid. Any deviation from the desired concentration is clearly indicated by a change in the sound heard in the instrument, and the operator is enabled to restore the concentration and at the same time the tone in the instrument to what is desired, by appropriate adjustment of the flow of diluting liquid into the circulating system of the final absorption tower.

**Absorption in Sulfuric Acid Nitration Processes.** — One of the most important absorption operations in all industry, from the standpoint of monetary value of the absorbed gases, is that of absorbing nitrogen oxides from the spent gases of nitration processes for the manufacture of sulfuric acid. The best known of the nitration processes is of course the chamber process, in which a gas mixture containing usually from 5 to 10 per cent $SO_2$ is treated with nitrogen oxides and atomized water (formerly, with steam) in a series of lead chambers. The reactions in the chambers result in the production of sulfuric acid and in the regeneration of the nitrogen oxides, which are not consumed. The gases from the final chamber, comprising the nitrogen oxides mixed with over 90 per cent of nitrogen, from 5 to 7 per cent of

oxygen and a trace (about 0.05 to 0.10 per cent) of $SO_2$, proceed to the Gay-Lussac towers for the absorption of the nitrogen oxides.  Probably the largest absorption towers used in any industry are the Gay-Lussac towers of the large-scale sulfuric acid plants.  At a small acid plant, the necessary Gay-Lussac tower space can easily be comprised in one tower.  At the larger plants it is customary to have two or three Gay-Lussac towers in series.  These towers are fed with 60° Bé. sulfuric acid, pre-cooled to a low temperature, preferably 30° C.; but at most chamber acid plants the acid cooling equipment is deficient, resulting in a temperature of from 40°–50° C. for the tower acid.

*Gay-Lussac towers* must be constructed of materials that will withstand the action of the acids and gases handled.  Formerly Gay-Lussac towers were built of sheet lead lined with brick walls laid dry or in "acid-proof" cement.  In some later installations the brick lining has been omitted, but the acid supplied to such a tower should be well-cooled, to avoid unduly rapid corrosion of the lead, as well as to effect better recovery of the nitrogen oxides.  Many Gay-Lussac towers have been built entirely of "acid-proof" masonry (brick laid in silica-silicate of soda cement) with omission of lead sheets, and such towers, though initially expensive, have been operated for many years with low maintenance and low depreciation expense.  Gay-Lussac towers formerly were packed with lumps of quartz or coke, but modern towers are nearly all packed with manufactured packers.

In a series of three Gay-Lussac towers, the cooled 60° acid, obtained from the Glover tower, is supplied to the final tower, the discharge from which (preferably after passing through a cooler) is supplied to the middle tower, and the discharge from it (also preferably after cooling) is pumped to the front tower.

*Absorption of Nitric Oxides.* — The discharge from any of the Gay-Lussac towers may be considered as a more or less dilute solution of nitrosyl sulfuric acid in 60° Bé. sulfuric acid.  The nitrogen oxides in the gases escaping from the last chamber exist chiefly in the form of NO and $NO_2$ in the proportions necessary to form the compound $N_2O_3$.  The principal reaction in the Gay-Lussac tower may therefore be written:

$$N_2O_3 + 2H_2SO_4 \rightarrow 2SO_2 \begin{array}{c} \diagup OH \\ \diagdown ONO \end{array} + H_2O.$$
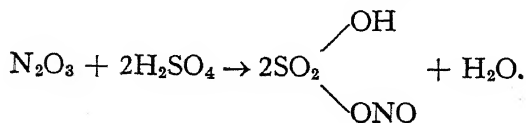
Sometimes $N_2O_4$ is also present, resulting in this reaction:

$$N_2O_4 + H_2SO_4 \rightleftarrows SO_2\begin{array}{l}\diagup OH \\ \diagdown ONO\end{array} + HNO_3.$$
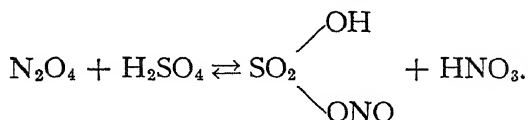
The proportion of nitric acid in the Gay-Lussac tower discharge is therefore dependent on the extent to which free $N_2O_4$ is present in the chamber-exit gases.

The acid discharged from the middle and final towers is known as "weak nitrous acid" or "middle acid," and the discharge from the front tower is called "nitrous vitriol." The acid discharged from the final tower normally contains nitrogen oxides equivalent to two or three ounces of sodium nitrate per cubic foot of acid; from the middle tower, 9 to 12 ounces; and from the front tower, 30 to 35 ounces. The acid and gases usually flow counter-current to each other, but occasionally a middle tower is down-drafted, to save flue construction. The normal recovery percentage of an average set of Gay-Lussac towers is from 82 to 86 per cent of the total nitrogen oxides in circulation.

The loss, from 14 to 18 per cent of the total "niter" in circulation, is made up by adding fresh nitrogen oxides, either as nitrate of soda or as oxidized ammonia gas, at the front end of the acid plant. The nitrous vitriol discharged from the front Gay-Lussac tower, containing the 82–86 per cent of the niter that is reclaimed, is supplied to the Glover tower, at the front end of the plant. Here it is mixed with the 53° Bé. chamber acid, and, thus diluted, it enters the Glover tower, and, coming into contact with hot sulfurous gases, releases its nitrogen oxides into the gas stream, to re-enter the chambers and to serve again as oxygen-carriers in the manufacture of sulfuric acid.

**Absorption in the Manufacture of Nitric Acid.** — The old method of making nitric acid is to heat nitrate of soda and 66° Bé. sulfuric acid, in definite proportions, in a cast-iron pot heated with coal or other fuel. The reaction involved is:

$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3.$$
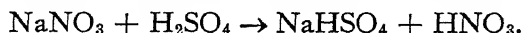
The sodium bisulfate remains in the pot, to be tapped out, while still molten, after the nitrogen compounds have been completely distilled off. The gases are conveyed to a cooler, and then to a

series of absorption towers, for the production of commercial nitric acid.

*Production of Nitrogen Oxides.* — According to modern methods, nitrogen oxides are produced, directly or indirectly, by the fixation of atmospheric nitrogen, with subsequent absorption of these oxides to yield nitric acid. The principal direct method of producing nitrogen oxides from atmospheric nitrogen is to heat air to a very high temperature by means of the electric arc — the Birkeland-Eyde process. The indirect methods of producing nitrogen oxides involve the preparation of ammonia, as a preliminary step, followed by a burning, or oxidation, of the ammonia. Any of the following processes may be used for the preparation of ammonia:

1. From cyanides, as in the Bücher process;
2. From aluminum nitride, as in the Serpek process;
3. From cyanamide, as in the Frank-Caro process;
4. By direct synthesis from hydrogen and nitrogen in the presence of a catalyst.

The last of the above four methods is rapidly superseding all others, including the niter pot method (in America at least), for the manufacture of nitric acid. In Norway, where power is very cheap, nitric acid in considerable quantities is made from nitrogen oxides produced with the flaming arc.

*Absorption Methods.* — The following factors determine the details of the absorption equipment and methods to be employed:

1. The concentration desired in the product;
2. The concentration of nitrogen oxides in the gas mixture;
3. Economic conditions prevalent at the site.

For some purposes highly concentrated water-white acid is demanded; and for other purposes weak acid or acid discolored with nitrogen oxides in solution is satisfactory.

Where the arc process is used, large volumes of a gas mixture containing only from 1 to 1.5 per cent of nitrogen oxides must be handled. The oxidation of ammonia yields a gas containing about 9 per cent of oxides of nitrogen. The denitration of reclaimed acids from the manufacture of high explosives produces nitrogen oxide mixtures in concentrations up to 15 and 20 per cent.

The relative availability and cost of different kinds of materials

of construction, the distance from markets, prevailing freight rates and other local economic conditions, influence the kind of absorption method to be chosen.

The absorption of nitrous gases may be accomplished by means of (*a*) water; (*b*) alkalies (solid or in solution); (*c*) concentrated sulfuric acid; (*d*) certain salts; (*e*) any one of the above mediums, preceded by liquefaction or concentration of the nitrous gases. The only method that will be considered here is absorption in water, because this is the method that is in use almost universally.

*Absorption by Water.* — The reactions governing the absorption of nitrogen oxides in water, as generally accepted, are:

(1)      $N_2O_4 + H_2O \rightleftarrows HNO_3 + HNO_2 + X$ cal.

(2)          $3HNO_2 \rightleftarrows HNO_3 + 2NO + H_2O - 18.4$ cal.

(3)      $2NO + O_2 \rightleftarrows N_2O_4 + 14{,}000$ cal.

The two phases represented by these reactions are gaseous and liquid. Since the reactions are reversible, the gaseous phase is subject to influence by variations in pressure, temperature and concentration, and, in its relation to the other phase, by variations in velocity. The influence of temperature is particularly important. For a complete discussion of this subject the reader is referred to Webb [10] whose deductions are that an increase in the temperature of the gases above atmospheric temperature, has the following disadvantageous effects:

1. It lowers the partial pressure and solubility of $N_2O_4$;
2. It diminishes the velocity of oxidation of the regenerated NO;
3. It increases the amount of $N_2O_3$ in the system;
4. It decreases the capacity of the absorption apparatus;
5. It increases the quantity of nitric acid evaporated;
6. It reduces the concentration of the nitric acid produced.

Webb concludes that 40° C. should be regarded as the maximum temperature for the inlet gases, and that the gases ought to be cooled to as near atmospheric temperature as possible, with 15° C. as the low limit, beyond which no material advantage can be derived.

*Cooling the Gases.* — There is little difficulty attached to the cooling of gases from the denitration of waste acids, or from

[10] H. W. Webb, "Absorption of Nitrous Gases," **1923**, p. 95 ff. Longmans, Green & Co.

niter pots, where the gas volume is small and the concentration of nitrogen oxides is high. The oxidation of ammonia, on the other hand, yields a large volume of gas at a temperature of about 600° C., while the arc nitrogen-fixation process yields a still greater volume of gas at temperatures above 1000° C. Special means must be provided for cooling such gases, prior to absorption.

The gases from ammonia converters are passed successively through a heat exchanger, through air-cooled pipes, and finally through water-cooled pipes. Gases from the arc process are conducted under boilers, where the bulk of the heat is utilized to generate steam. The gases issue from the boilers at between 150° and 200° C., and are then conducted through long air-cooled and water-cooled mains.

In the absorption of nitrogen oxides in water, the degree of oxidation in the gases cannot be overlooked. At most plants the gas is initially chiefly nitric oxide, which must be oxidized to the tetroxide before entering the absorption towers. This oxidation is an exothermic reaction, which tends to increase the temperature, and coolers must be provided to counteract this tendency.
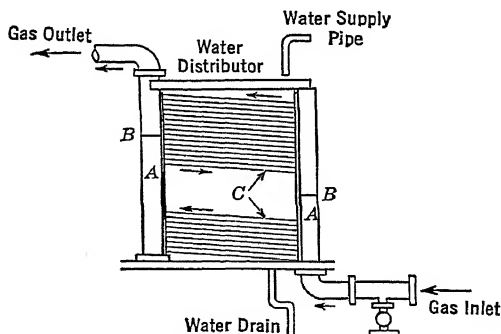


FIG. 134. Hart Condenser. *A*—Gas Headers; *B*—Partitions. *C*—3-inch Glass Tubes.

*Hart Condenser.* — For niter-pot gases the cooler most extensively adopted is the Hart Condenser (Fig. 134). This consists of rows of slightly inclined and parallel tubes of heat-resisting glass, connected to vertical gas headers made of stoneware. The glass tubes are cooled by water trickling over them, which is supplied from above. The gas from the inlet header passes through the glass tubes to the outlet header. Since the gases contain some

moisture, condensation of weak nitric acid occurs in the tubes, and this drains by gravity to a suitable receptacle. At some plants, the Hart condenser has been superseded by S-bend condensers made of pure fused silica or of silicon-iron alloy. After cooling, the gases are conducted to a series of stoneware absorption-towers, similar to those used in the manufacture of hydrochloric acid (Fig. 132). The towers were formerly packed with quartz, but nowadays manufactured packers are used.

*The ammonia oxidation process* for the manufacture of nitric acid consists in passing gaseous ammonia, mixed with air in the proportions of about 1 : 9.5, through a converter containing a catalyst made of platinum gauze. The catalyst is usually cylindrical in shape, and the cylinder is closed at its lower end by a silica plate. The ammonia-air mixture, after passing through a heat exchanger, in which it is preheated by the hot oxidized gases, enters the top of the catalyst, and passes through the meshes of the platinum gauze, which, after its initial ignition, is heated automatically to incandescence by the reaction, and the oxidation of the ammonia to oxides of nitrogen takes place. The oxidized gases, heated by the reaction to a very high temperature, proceed to the heat exchanger, where they are partially cooled, and are then conveyed through chrome-iron pipes to a gas-cooler consisting of banks of superposed horizontal pipes connected by U-bends, and cooled by trickling water supplied from above. Beyond the gas-cooler, sufficient air is admitted to the gas stream to dilute the concentration of nitrogen oxides (originally 9.5 per cent), to 7 per cent, thus facilitating the oxidation of nitric oxide. The gas mixture, impelled by a gas fan, then proceeds through oxidizing towers, of such capacity that four minutes are required for the passage of the gas. The cooled and thoroughly oxidized gases then pass through a series of absorption towers. At the large modern works these are made of chrome-iron, are 10 ft. in diameter and over 50 ft. high and are packed with manufactured packers. The number of towers provided is such that the gas will consume ten minutes in passing through. The last tower of the series is fed with water in recirculated fashion, and the overflow passes forward to the next tower in the series, and so on, all of the towers being fed with re-circulated liquid passed over and over again through the same tower, with the surplus passing automatically to the next forward tower in the series. The discharge from each tower is thus stronger in nitric

acid than that of the one beyond it in the series and the first tower discharges acid at from 50 to 60 per cent $HNO_3$. The recirculated liquids, upon escaping from a tower, pass through a cooler before being re-pumped. The distribution of the liquid at the top of the towers is very important. Spray nozzles producing a solid cone of spray (not a hollow cone) have been found satisfactory.

It has been calculated that with gases containing 10–15 per cent $NO_2$, approximately 90 cu. ft. of free space within the packed space are required per pound of $N_2O_4$ per minute. The gross tower space required will vary with the percentage of free space afforded by the type of packer employed. With a packer having 70 per cent of free space, the gross tower space provided should be 25 cu. ft. per ton of 100 per cent $HNO_3$ produced per week, using gas containing 10–15 per cent $NO_2$.[11]

*Comparative Costs.* — A set of eight small absorption towers, as used in the niter-pot method, erected, will cost, according to Webb,[12] about $10,000 and, as each tower 3 ft. in diameter and 13 ft. high corresponds to a yield of 3.6 tons of 100 per cent nitric acid per week, the capital expenditure for such an absorption equipment is about $350 per ton of $HNO_3$ per week. With the adoption of large towers, as in modern practice, it would be natural to assume that the necessary capital expenditure per unit of product would be materially less. However, the concentration of nitrogen oxides in ammonia oxidation gases is so much lower than that of niter pot gases that a much greater volume of tower space is required, at even greater expenditure of capital than for niter-pot systems. At European nitric acid plants using the ammonia oxidation process, the cost of the absorption equipment has been placed at about $650 per ton $HNO_3$ per week. The ammonia oxidation equipment, including platinum gauze, converters, and chrome-iron or aluminum pipes, is also more expensive than niter-pot equipment. The reduced costs of the ammonia oxidation process, therefore, as compared with the niter pot method, are not realized through cheaper equipment, but rather through the elimination of the waste of concentrated sulfuric acid and the reduction in amount of labor employed, combined with the greatly reduced expense for raw material. Anhydrous ammonia can be purchased, at most points in the

[11] Webb, *op. cit.*, 178.
[12] *Loc. cit.*

eastern part of the United States, for about six cents per pound $NH_3$, delivered. The large manufacturers of nitric acid produce their own synthetic ammonia, and their cost figure is undoubtedly considerably less than six cents per pound. Even at six cents the ammonia equivalent of a pound of nitrate of soda would cost about 1.27 cents, as compared with the actual price of a pound of nitrate of soda, delivered to interior points in the eastern part of the United States, of about 2.25–2.40 cents. If we assume that the value of a pound of nitrate of soda, with sulfuric acid, fuel and labor added, is 2.70 cents, cooked in a niter pot, and that a pound of synthetic ammonia costs the large producer four cents, delivered (equivalent to 0.85 cent per pound nitrate of soda), it is evident that the nitrogen oxides by the pot method cost over three times as much as by the ammonia oxidation process, for the large manufacturer of nitric acid.

### PROBLEMS

59. A nitration-process sulfuric acid plant burns 40,000 lbs. of brimstone per 24 hours, and produces burner gas containing 10 per cent of $SO_2$ by volume. Assuming that all of the $SO_2$ is condensed to sulfuric acid, and disregarding the volume of the nitrogen-oxygen compounds and that of the residual moisture, what volume of gas, at 50° C. and 740 mm. pressure, will pass through the Gay-Lussac absorption towers per minute?

60. Anhydrous ammonia can be purchased at a delivered price of 6 cents per pound, and can be burned to produce nitrogen oxides at an oxidizing efficiency of 90 per cent. Nitrate of soda (96 per cent $NaNO_3$) can be purchased at a delivered price of 2 cents per pound, and can be used to produce nitrogen oxides with an efficiency of 99 per cent. What are the prices per pound of nitrogen in the nitrogen oxides produced from the two raw materials?

61. An absorption system comprises five towers, each 4 ft. in inside diameter and each capable of containing 15 vertical feet of packing. The frictional coefficients for various styles of packing, wet with circulating liquid, are, per square foot of area per foot of height:

1. For $3'' \times 3''$ diaphragm rings, stacked in staggered courses........ $58 \times 10^{-7}$
2. For $3'' \times 3''$ diaphragm rings, dumped in...................... $63 \times 10^{-7}$
3. For $3''$ quartz, dumped in...................................$139 \times 10^{-7}$

What pressure will be required, for each of these three styles of packing, wet with circulating liquid, to force 1,000 cu. ft. of gas per minute through the absorption system?

62. Gas from a pot-and-muffle hydrochloric acid retort, containing 30 per cent hydrogen chloride, can be satisfactorily absorbed when the velocity of the gas in the absorption towers is one linear foot per second, with total period of contact with absorbing liquid of 30 seconds. What volume of packed tower space and size of tower will be required to accommodate these conditions, at a plant producing 300 cu. ft. of gas per minute, using packing material that provides 50 per cent free (unoccupied) volume?

## ELECTROLYSIS

### ELECTROLYTIC CELLS FOR THE PRODUCTION OF CAUSTIC AND CHLORINE

#### L. D. VORCE, D.Eng.

**Theory of Decomposition by Electrolysis.** — According to the ionic theory, if we dissolve salt in water it will be dissociated into its components parts, $NaCl = Na + Cl$. But we know that the metal sodium cannot exist as such in the presence of water, but would decompose it with the formation of sodium hydrate, liberating hydrogen gas.

Since we find that this does not occur, the explanation is that, during dissociation, the sodium particle is charged positively and the chlorine particle negatively, thus preventing these elements from acting as they normally would. Hence we must visualize the sodium particle not as $Na$, metallic sodium, but as $Na^+$, sodium ion, and the chlorine not as $Cl$, free chlorine, but as $Cl^-$, chlorine ion.

These ions exist in that form until they meet conditions permitting the discharge of their electric charges. This happens when they come in contact with the electrodes in an electrolytic cell, where the sodium ion may discharge its positive charge to the negative pole and appear as metallic sodium capable of decomposing water, and in like manner the chlorine ion with its negative charge coming into contact with the positive electrode gives up its negative charge and appears as elementary or gaseous chlorine.

Thus it will be observed that the electric current impressed upon the solution of sodium chloride has performed the function of decomposing a chemical compound into other substances having properties varying widely from the original salt in solution. This is a typical illustration of electrolysis and the use of the electric current to perform chemical changes.

If in the above example, only those ions in immediate contact with the electrodes were affected, the operation would stop as

soon as those ions had discharged their electric charges. This, however, is not the case, for as long as the current is passing through the solution there is a constant migration of ions, the negatively charged toward the positive pole and the positively charged toward the negative pole. The various ions have differing rates of speed of migration and in many operations steps must be taken to prevent this property from interfering with the efficiency of the separation which is sought.

*Decomposition Voltage.* — If the heat of formation of a chemical compound is known we can calculate the electrical energy required to decompose it.

In the case of sodium chloride the heat of formation in the solid state is 97,690 calories, which is the amount that would be liberated during the formation of 58.46 grams of sodium chloride from its elements sodium and chlorine. Naturally an equivalent amount of heat would be required to decompose the 58.46 grams in the solid state. As one calorie equals 4.1834 joules, 97,690 calories is equal to 408,676 joules. By Faraday's law we know that the amount of electrical current in coulombs necessary to deposit a gram equivalent of any chemical element is 96,540. As joules equal amperes times volts times seconds, and as coulombs equal amperes times seconds, joules divided by coulombs equal volts. Therefore the potential required to decompose sodium chloride into sodium and chlorine would be 408,676/96,540 = 4.23 volts.

This is the theoretical decomposition voltage for solid sodium chloride. Since however, the decomposition must be carried out with the fused salt at a temperature of 772° C., a large amount of heat is absorbed by the salt as specific heat and this operates to reduce the decomposition voltage. Starting at room temperature of 15 degrees, the amount so absorbed is 9480 calories, and this reduces the decomposition voltage so that it actually is 3.81.

When however, the electrolysis is carried on in an aqueous solution of sodium chloride, other factors must be taken into consideration, as other decompositions and recombinations of elements occur, according to the reaction:

$$NaCl + H_2O = NaOH + Cl + H.$$
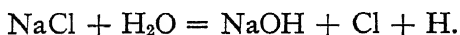
In this reaction there has been decomposed one molecule of salt and one molecule of water and at the same time one molecule

of sodium hydrate has been formed.   To the heat of formation
of the sodium chloride must be added that of the water, since
they were both decomposed, and from this sum must be taken
the heat of formation of the sodium hydrate, since that was
formed and its heat liberated.   Then proceeding as before we
obtain 2.28 as the decomposition voltage of sodium chloride in
aqueous solution.   It is customary to use the figure 2.3 for con-
venience.

*Current Efficiency.* — It has been stated that 96,540 coulombs
will deposit one gram molecule of any element.   Since coulombs
are ampere seconds, by dividing that figure by 3600, seconds times
minutes per hour, we find that 26.8 ampere hours will produce
23 grams of sodium equivalent to 40 grams of sodium hydrate
in one hour, or one ampere will produce 1.493 grams per hour.
By as much as the amount produced falls below this figure in
the operation of a cell the current efficiency will fall below theory
or 100 per cent.   For reasons shown later it is impossible to
realize 100 per cent and the current efficiency of any cell is the
ratio of the actual production to the theoretical yield.

*Power Efficiency.* — As the energy impressed upon the oper-
ation has two components, amperes and volts, we have to con-
sider both current efficiency and energy or power efficiency.   It
was shown that the decomposition voltage of sodium chloride in
water solution is 2.28.   If the operation could be carried out at
this voltage and the current efficiency was 100 per cent, then we
could say the cell was operating at 100 per cent power efficiency.
As a matter of fact it is not possible to achieve this figure.   Not
only is the current efficiency lower than 100 per cent but the
voltage required in operating a cell is always higher than the
theoretical voltage of decomposition due to ohmic resistance in
connections, diaphragm and electrolyte.   If then we find that
the voltage of the cell is 3.5 volts and the current efficiency is 95
per cent, then the energy or power efficiency is found by multi-
plying the actual current efficiency by the theoretical decom-
position voltage and, dividing it by the actual voltage.   In the
above case the power efficiency will be

$$\frac{95 \times 2.28}{3.5} = 61.88 \text{ per cent.}$$

*Diaphragm Cells.* — As chlorine is liberated at the anode, and
sodium at the cathode, or caustic soda and hydrogen if water is

present, it is necessary to keep these decomposition products of the salt separated, otherwise recombination will take place with loss of the product. This is accomplished in several ways, the most common of which is to insert a porous diaphragm, such as asbestos paper, between the two electrodes forming two compartments of the cell. Ions and molecules will diffuse through such a porous diaphragm, which will also allow free passage of the electric current. If the diaphragm is entirely covered with brine or other liquid it is known as a submerged diaphragm. If brine is in contact with only one side of the diaphragm, as is true in some types of cell, it is known as an unsubmerged diaphragm.

*Decomposition Efficiency.* — In most diaphragm cell operations in which a salt is being decomposed there will be more or less of the undecomposed salt carried along through the diaphragm with the product or products of the electrolysis. With a sodium chloride cell, for example, the brine which is fed to the cell is at about the saturation point, containing 26.4 per cent sodium chloride, in order to keep the ohmic resistance as low as possible. The passage of the solution through the diaphragm is governed by the thickness and density of the diaphragm and by the hydrostatic head of the solution in the cell. If then, more sodium chloride passes through the diaphragm in a given period of time than the current impressed on the electrodes can decompose, it follows that some of it will remain in the effluent, and the term *decomposition efficiency* has been used to cover the percentage decomposed. If, for example, we pass a sodium chloride solution containing 300 grams sodium chloride per liter through a cell and the effluent carries 120 grams per liter of sodium hydrate, by calculation we find that in producing 120 grams of sodium hydrate 175 grams of sodium chloride have been decomposed, then $175/300 = 58.03$ per cent is the decomposition efficiency. If it were possible so to operate a cell as to decompose all the sodium chloride without other disadvantageous factors creeping in, it would be of immense importance, as it would obviate the necessity of recovering and washing free from caustic the undecomposed salt. Several things prevent this.

If we dilute the solution to the point where no more of the salt passes than the current will decompose, the conductivity of the solution is lowered and the ohmic resistance to passage of the current results in higher voltage and lower power efficiency and a possible decomposition of water. If, on the other hand,

we keep the solution saturated and thicken the diaphragm to a point where it will permit only the passage of sodium chloride equivalent to the current used, the added resistance of the diaphragm increases the voltage. Finally, if we hold the solution saturated and keep the diaphragm of a proper thickness so that no undue resistance is caused therein, we might increase the amount of current to the degree necessary to decompose all the sodium chloride passing. Here, however, we encounter another difficulty. The nature of the anode is such that the attempt to impress the high current density required also increases the voltage of the cell, and moreover greatly shortens its life by the more vigorous oxidation which is set up. For this reason it is necessary to balance the decomposition voltage with other factors from an economic standpoint. With high power cost and low evaporating charges the decomposition should be low. When power cost is low and fuel is expensive, resulting in high evaporation cost, the decomposition efficiency should be high as this results in high current efficiency.

*Recovery of Decomposition Products.* — When a salt solution is electrolyzed and the chlorine ion gives up its negative charge and becomes chlorine gas, the greater part rises to the surface and may be removed, but a part remains in solution in the electrolyte. When the sodium ion gives up its electrical charge, becoming metallic sodium, it promptly decomposes a molecule of water according to the well known reaction, $Na + H_2O = NaOH + H$.

It is understood that we are seeking to produce the two products, chlorine gas and sodium hydrate, and possibly the hydrogen. The chlorine gas is readily collected since for the greater part it leaves the solution and may be drawn off by suitable means. The caustic soda, on the other hand, is in solution along with the salt which percolates through the diaphragm. If the caustic could be withdrawn as fast as formed at the negative pole, the task would be easy. There are difficulties and limitations in the operation which prevent this. The electrolyte is free to move and such action is accelerated by the heat liberated by the current in overcoming the resistance to its passage, and the caustic is free to combine with such chlorine as is in solution and reaches the cathode with the formation of sodium hypochlorite. $2NaOH + Cl_2 = NaCl + NaOCl$. Moreover, by the formation of the caustic, there has been introduced into the electrolyte the base $NaOH$, which is also subject to ionization

and electrolysis according to the reaction, $NaOH = Na^+ + OH^-$, producing another positive sodium ion, and the negative hydroxyl ion.

To the extent that this takes place the efficiency of the cell is reduced. It therefore becomes necessary to devise some means of preventing this so far as possible. In so far as this can be done, the process becomes successful. Several methods of minimizing this recombination of the elements may be employed, and this brings us to the practical consideration of the subject.

Before taking up the development of electrolytic caustic-chlorine cells, however, it is wise to consider that so far we have limited our theoretical consideration to a very narrow field. It will be obvious that there are a very large number of substances which lend themselves to electrolytic treatment for the separation of one or more constituents, which may only be indicated in this chapter. These include the entire range of electro-deposition of metals (cathode products), either for surface effect as in nickel, chromium and silver plating or for massive separation as with copper refining, aluminum production, or in the separation of gold and silver from the baser metals. Likewise there are many anode products to be made, bromine, iodine and a considerable range of oxidation substances, each of which deserves a chapter of its own. The general principles governing the production of these products are the same as for the production of chlorine and caustic soda.

**Electrolytic Cells for the Production of Caustic and Chlorine. —** The practical application of the principles of electrolysis to commercial industry became possible only when the necessary apparatus and materials of construction had been developed. In fact, generally the tools for an operation are the result of the call for them. The products of the electrolytic decomposition of salt, namely, chlorine and caustic soda, are highly corrosive in their nature and only by a great deal of experimental work has it been possible to develop materials for construction which would endure to the extent necessary to prove profitable. It is only within the last few years that cells have been developed which are able to stand up for longer than a few months. Not until the manufacture of artificial graphite had been developed was an anode material available which was not either too expensive or too short lived.

Since commercial operations call for a very large amount of electric power, there could be no considerable progress prior to the development of the dynamo and the gradual lowering of the power cost to a point where electrolytic caustic could compete with that made from soda ash.

*Development of Cells.* — The important steps which have led to modern cell construction can best be shown by the historical development of the art. The work of Sir Humphrey Davy in 1807 in preparing the metals sodium and potassium electrolytically from their compounds is the starting point, followed by the fundamental researches of Faraday which were published in 1833.

Most inventions of importance get their introduction to the public through the Patent Office. The first patent of record in the art is that of Chas. Watt, 1851, who patented the preparation of chlorine, soda, sodium hypochlorite and chlorate from sodium chloride, using a cell with submerged diaphragm. His ideas were far ahead of the facilities available at that early date.

The next patent of importance is that of C. A. Faure, 1872. In this is first disclosed the idea of an unsubmerged cathode, which has now been adopted in most diaphragm cells. Being so far ahead of any chance of practical application it was overlooked until it was again promulgated by Allen and Moore in 1897.

The first patent issued in this country for an electrolytic cell was in 1883, to A. L. Nolf, a Belgian, and not until 1890 was a cell patented by an American, I. L. Roberts. While the Roberts cell was later given a commercial trial at Niagara Falls, the first commercial production of caustic is due to the work of E. A. LeSueur, whose patents appeared in 1891. A description of the plant built at Rumford Falls, Maine, by C. L. Parsons, is to be found in Vol. 20, Jour. Amer. Chem. Soc., and a further interesting account by Barton, A. I. C. E., Vol. 13, part 1.

The gradual development of cells for the electrolysis of sodium chloride brines illustrates: (*a*) the utilization of a great variety of materials of construction of the cells; (*b*) change of design for the production of a purer product and a higher yield; (*c*) increased capacity and increased life of the cell, (*d*) reduction in cost of the cell and cost of labor for repairs and replacement; and (*e*) reduction of floor space required.

The development of a number of typical cells will illustrate these principles.

*The LeSueur Cell.* — According to Barton, the original LeSueur cells were of bell jar construction with asbestos diaphragms approximately horizontal. The anodes were of gas retort carbon
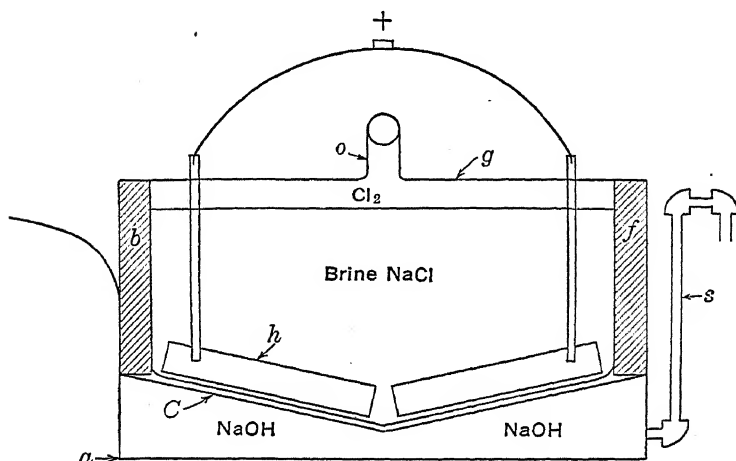


FIG. 135. Le Sueur Cell.

and were cast in lead, a projecting portion coming through the top of the bell jar for positive connection. They were intended to take 100 amperes each and were run in parallel in iron tanks, which were connected in series. The diaphragms required frequent changing and they were soon replaced with a *second cell design* in which square boxes 24 × 24 × 24 inches replaced the bell jars. The upper third of the outside was of slate with a slate cover, and a wooden leg at each corner supported it from a wooden bottom. Around the open space, asbestos paper was wound and outside of this, wire netting constituting the cathode which made contact with the iron tank, which held the cathode. The anodes, as before, consisted of gas carbon with the ends cast in lead, and in addition the space between the central anode proper and the asbestos was filled with lumps of broken retort carbon, the object being to hold the diaphragm paper against the wire netting and bring the anode surface closer to the cathode.

The *third type of cell* was a slate box with gas retort carbon anode but no packing between the anode and the diaphragm. The larger ones were made 36 inches long, 6 inches wide and 18 inches deep. The *fourth type* of cell constructed was a distinct

departure from the previous forms.   It was a large unit and was contained in a cathode tank, 9 feet long, 5 feet wide and 18 inches deep.   A wooden platform of $4'' \times 6''$ lumber was laid in the bottom of the tank, on this a grid of iron made of $\frac{3}{8} \times 1\frac{1}{2}$-inch bars was laid and part of the bars were extended and bolted
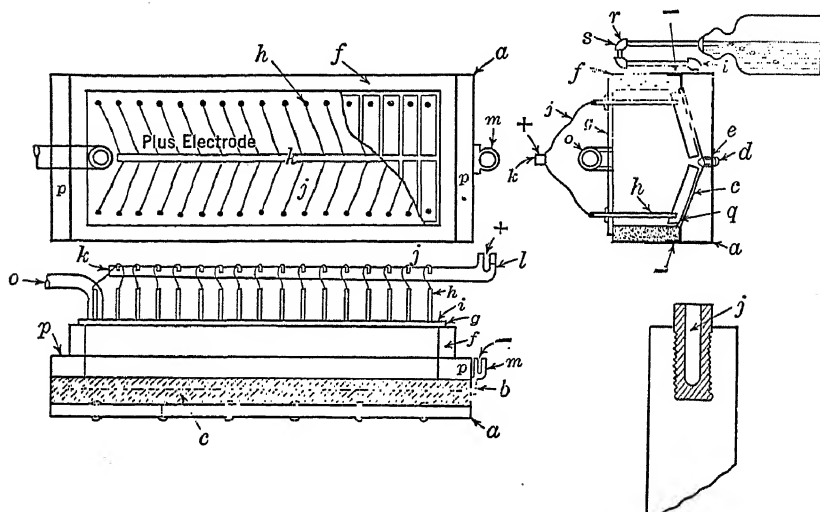


Fig. 136.   Side and Elevation of Le Sueur Cell.

to the tank for contact.   These irons were inclined so that there was a pitch of 2 inches to the foot.   On top of these irons a wire netting was placed to act as the cathode proper, and on top of this a diaphragm of asbestos paper was laid.   The side walls of the anode compartment were made of red brick and the diaphragm was cemented in with quick hardening cement.   The covers were of slate and the anodes of platinum wire.   With the necessity to economize on the platinum used as anodes it became necessary to run at a very high anode current density with the result that the voltage was 5.5 to 8 volts.

*The McDonald Cell.* — This was designed from the third type of LeSueur cell.   It consists of a rectangular steel tank having two perforated steel cathodes running the long way of the tank and dividing it into three parts.   The center is the anode compartment, the perforated plates are lined with the asbestos diaphragm, and it is provided with a lid carrying a series of

vertical graphite anodes which are much cheaper than platinum and better conductors than gas retort carbon. The outer divisions serve as cathode compartments. Brine is fed continuously into the anode chamber, a part flows through and out from an exit at the end of the cell to be resaturated and returned, while a p o r t i o n percolates through the diaphragm and undergoes electrolysis. New diaphragms offer but little resistance to the flow of the electrolyte through them, and under such conditions t h e hydrostatic pressure difference is reduced by working with the cathode chambers more or less full of electrolyte, that is, the cell is operated as a submerged cathode cell. As time goes on and the diaphragms became clogged up, the level of the cathode liquor is lowered by adjusting the overflow from the cathode chamber until finally it is transformed into a cell of unsubmerged cathode type. Naturally a cell working under such varying conditions could not be expected to show high efficiency.



FIG. 137. Section of Allen-Moore Cell Showing: $A$ — Graphite Anode; $B$ — Unsubmerged Cathode Consisting of Iron Grid Supporting Asbestos Diaphragm.

The *Allen-Moore Cell.* — This cell was developed f r o m experience with the LeSueur cell and was the first cell in commercial operation in which the outside of the cathode was unsubmerged. It consists of a concrete form

of U shape upon both sides of which are clamped the iron cathodes with asbestos paper acting both as diaphragm and gasket making the joint between cathode and frame.    The anodes consist of slabs of graphite placed horizontally in front of the cathode and jointed to vertical carbon posts which pass through the top of the cell for current connection.    Outside of the cathode is a cover box on each side for protection of the cathode from salting and for the conservation of the hydrogen.    The negative connection is made through the protecting covers to the cathode and connection to the anode is made by copper wires immersed in mercury in the top of the vertical carbon parts.    The cell was designed to carry 1500 amperes current.    It will be seen from the design of this cell that only the exterior face of the carbon is effective.

The advantage of the unsubmerged cathode consists in the fact that the caustic soda as soon as formed flows to the bottom of the cathode compartment thus preventing in a measure diffusion of caustic into the anode compartment.

*The Nelson Cell.* — This cell was developed from experience with the McDonald cell at the Warner Chemical Company plant in Carteret, N. J., and is shown in patent U.S. 1,149,210.    It consists of a rectangular steel tank of $\frac{1}{4}''$ metal which forms the body of the cell (Fig. 138 and Fig. 139).    In this is mounted a U-shaped cathode plate of perforated steel, *5*, which also acts as the form for the anode compartment.    The asbestos diaphragm, *8*, consists of a sheet of asbestos paper fitted closely to the cathode and in addition a sheet of asbestos cloth is placed inside the paper.    The top edges of paper and cloth fold back on supporting angles, *6*, fastened to the top edges of the cathode which also serve to distribute the current to the cathode.    The cathode rests on angles riveted to the inside of the tank.    The ends of the diaphragm are made tight by placing a wood form down in the cathode U a few inches from the ends of the container box and filling the spaces with cement, *18*.    An inverted rectangular box of slate slabs, *12* and *13*, closes the top of the anode compartment and also acts as a support for the graphite blocks which form the anode.    These blocks are 4 × 4 × 17 inches, and into the top of each block is screwed a graphite rod, *11*, $2\frac{1}{2}$ inches in diameter and 12 inches long.    The blocks are supported in place by short glass rods passed through holes in the rods and, to prevent the gas from escaping, are luted with putty.    After the anode is in

position in the slate box, the space from the slate to the edge of
the container tank is made tight with cement, $E$.   The positive
terminal is connected by means of a flat copper bar, *15*, bolted
to each of the fourteen anode rods, and a flat copper plate, *7*,
riveted to the cathode performs a similar service for the negative

NOTE:  LENGTH OF CELL 80" CONTAINS 14 ANODES

15  Copper Bus Bar Connecting
        14 Anodes $P$                                    $A$

14  Gas Outlet of Glass Tube
        at End of Cell $O$
        Putty $N$                    Slate Top Piece
                                         $B$              13

11  Round Anode $M$                    Slate Side Piece
                                              $C$         12

    Copper Terminal
    at End of Cell $L$               Bolts at Ends of Cell  16

    Putty $K$                        Copper Terminal
                                     at End of Cell        9

18  Cement $D$                       Cement $E$

6   Angle Irons $G$

10  Square Anode                     Perforated Steel
                                     Diaphragm $F$         5

                                     Asbestos Diaphragm
                                          $J$             8

                                     Diaphragm Support
                                     at Ends $I$          9

                                     Steel Tank
                                          $H$             1

FIG. 138.   Section of Nelson Electrolytic Cell.
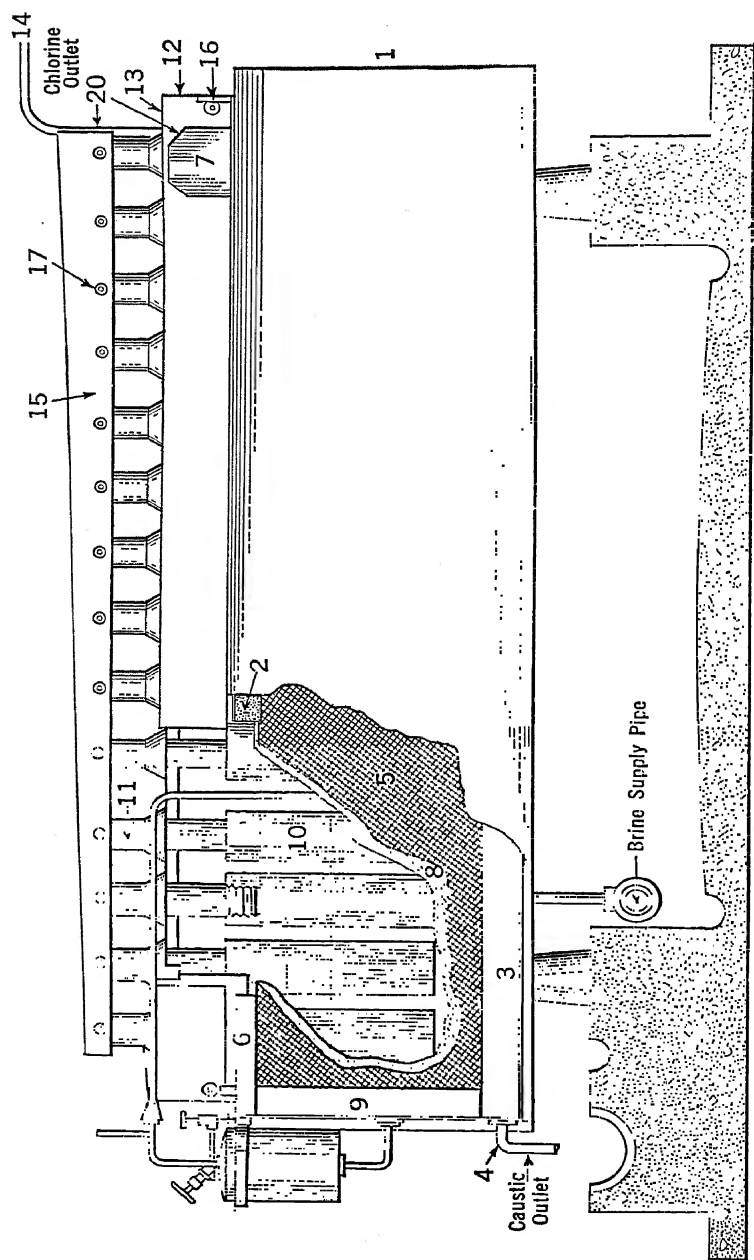
FIG. 139.  Nelson Electrolytic Cell.

terminal. An automatic feeding device serves to regulate the level of the brine in the cell. This consists of a globular glass bulb placed in an inverted bell jar, the tubulure of which is connected to the anode compartment. Above the center of the bell jar is an iron rod projecting from the end of the cell and the rubber hose which delivers the brine to the cell passes between this rod and the float bulb supported by the brine. The delivery tube then passes to a glass tube leading into the top of the anode compartment. When the brine in the cell reaches the predetermined level, the buoyancy of the bulb compresses the rubber tubing and cuts off the flow of brine. The caustic effluent escapes at the end of the cell at the bottom, as the cathode runs unsubmerged. In replacing diaphragms it is necessary to remove the graphite, break the cement seal and remove the paper and cloth and rebuild while the cell is in position. The cell has a normal capacity of 1000 amperes and the starting voltage is from 3.5 to 3.7.

The U-shaped cathode plate of this cell with the asbestos diaphragm constitutes a much simpler design than previous cells, permitting operation with unsubmerged cathode, and giving large cathode surface in a relatively small space.

*The Townsend Cell.* — This cell is similar in general design to the Allen Moore cell except that it is made in larger units carrying as high as 5500 amperes. The essential feature is the employment of oil in the cathode compartment to receive the caustic as fast as formed at the cathode, with the idea of preventing diffusion back into the anode compartment. The caustic solution, being heavier than the oil, drops to the bottom of the cathode compartment and is drained off. Essentially the same advantages are gained by this method of operation as by the unsubmerged diaphragm. The amount of caustic in the effluent is somewhat higher than in most diaphragm cells.

*The Billiter Cell.* — This is a diaphragm cell of foreign design. As distinguished from those already mentioned, it is flat and consists of an iron tank approximately four feet wide by seventeen feet long. Fastened to the inside walls near the bottom are projecting flanges supporting a flat iron grid upon which lies the cathode proper of either wire gauze or perforated metal. The diaphragm consists of an asbestos cloth sheet laid upon the cathode and upon this is laid an inch and a half of barium sulfate mixed with asbestos fiber. A concrete extension of the sides of

the tank carries a cover of slate or concrete from which depend the leading-in rods of graphite 2″ diameter by 14″ long. The lower ends of the rods are screwed into the ends of the 24 slabs of graphite which are 7″ wide, 42″ long and 2″ thick. These slabs are supported 2″ above the diaphragm, the distance being great enough to prevent disturbing the diaphragm material by the evolution of the chlorine. Connection is made from the top of each leading-in rod to a bus supported above the cell. Originally 24 brine inlets were provided in the cover of the cell but this was later reduced to a single brine feed. Owing to the large gap between anode and cathode and the thickness of the diaphragm, the voltage of the cell is higher than usual. It is expected to operate at 4.2 volts, at 3300 amperes, but will run nearer to 4.5 to 5 volts. While such a cell runs at a satisfactory current efficiency and with a caustic content in the cell liquor greater than most diaphragm cells owing to the depth of brine allowable and thickness of the diaphragm, the power efficiency is low, at 95 per cent current efficiency and 5 volts being only 43.7 per cent. In addition, the flat design calls for much greater floor space. The factor of floor space may be realized from the fact that in one plant each bay of 17 Billiter cells carrying 56,100 amperes has been replaced with 216 cylindrical cells carrying 216,000 amperes, nearly four times as much product being obtained from the same floor space, and at a power efficiency of 60 per cent.

*Mercury Cells.* — In all the cells so far described the attempt to prevent recombination of the products of decomposition has been by interposition of a diaphragm, generally of asbestos cloth or paper, between the anode and cathode.

In the mercury cell no diaphragm is used, the sodium being absorbed in the mercury which is used as cathode, forming sodium amalgam from which the caustic may be formed by treating the amalgam with water. It has been found that there is a very definite limit to the amount of sodium which can be amalgamated without introducing difficulties. The sodium-laden mercury must be removed from the electrolyzing compartment and treated with water in a separate chamber, hence, if an excess of sodium is absorbed, making the amalgam too thick to flow easily from the electrolyser, the operation is blocked. Moreover, with an excess of sodium in the amalgam there is a tendency to the formation of caustic soda in the electrolyzing chamber, with the liberation of hydrogen which contaminates

the chlorine. In practice the concentration of sodium in the mercury is not allowed to exceed 0.05 per cent. The greatest advantage of the mercury cell is in producing pure caustic without salt contamination. The disadvantage is the high investment cost and high voltage, as in this cell no voltage reduction is available from caustic formation. Only two mercury cells of importance have been operated in this country.

*The Castner Cell.* — This consists of a large slate box four feet square by six inches deep, divided by two vertical partitions into three equal compartments. These partitions stop short of the
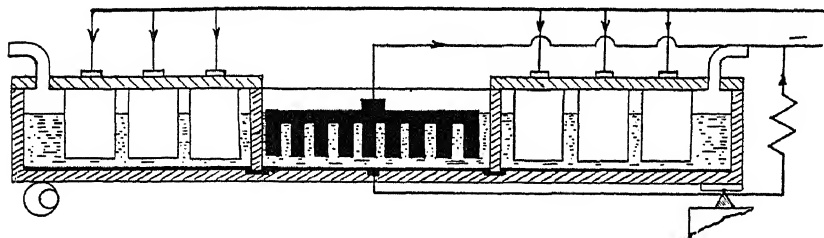


FIG. 140. The Castner Cell.

bottom by $1/16''$ and there is a shallow groove under each partition so that the mercury placed on the bottom can flow from one compartment into another. In the two outer chambers the mercury acts as cathode, and carbon anodes securely connected into the top of the cell reach within $1/2''$ of the mercury. In these two compartments the brine is circulated. The center chamber is filled with water in which is suspended an iron grid as cathode. One side of the cell rests on a fulcrum and at the other is an eccentric roller revolving at a slow speed so that the cell is alternately raised and lowered and the mercury moves alternately from one anode compartment to the center, while that in the center, denuded of its sodium, moves to the other anode compartment. If the full current were allowed to pass through the denuding chamber it would cause oxidation of the mercury and consequently a part is shunted around to the outgoing conductor.

*The Whiting Cell.* — The feature of this cell consists in automatic intermittent removal of the amalgam from the electrolyzer. The cell consists of a shallow cement box, divided by a partition into electrolyzer and denuding chamber. The electrolyzer itself

is subdivided by long glass partitions into five compartments, each containing its own graphite anode and provided with a separate valve through which the charged mercury can flow into the denuding chamber. These valves are alternately opened and closed by means of cams attached to a slowly revolving horizontal shaft. The amalgam rapidly passes out into the alkaline chamber (being replaced by fresh mercury from a constant level supply) and flows down by gravity through a series of channels in graphite slabs where it is short circuited and completely denuded of sodium, pure mercury arriving at the bottom. This is pumped up again by a cup wheel to the level of the electrolyzer. A cell 6 feet square takes 1200 to 1400 amperes. About 4 volts are required. Caustic soda solution of 20 per cent strength is produced but it can be carried to 40 per cent if desired. About 375 pounds of mercury are required per cell.

An improvement on this cell has been made by A. Sorenson by making the flow of mercury continuous instead of intermittent.

*The Acker Cell.* — Still another distinct method of electrolyzing salt consists in the use of a bath of fused metal such as lead. This obviates the necessity of using a diaphragm, and in this respect is similar to the mercury cell. As a high temperature is needed, fused salt must be employed. In the Acker cell the fused salt is electrolyzed in a cell of cast iron lined with magnesia bricks. The cathode covering the bottom of the cell is of molten lead. On this rests a 6″ layer of fused salt, into which dip four anodes of graphite attached to graphite rods passing through the roof of the cell. These rods are coated with fire clay and cement for protection from the hot gases. The lower surface of each anode is 6.5 sq. dm. and each anode takes 2000 amperes, or 8000 amperes for the cell. The gas drawn from a cell like this runs low in chlorine owing to the difficulty of maintaining tight joints, and has to be used in special bleach-making apparatus like the Hasenclever.

The sodium-lead alloy leaves the electrolysis cell and enters a smaller chamber where it is acted on by a jet of steam at 40 pounds pressure. This oxidizes the sodium to sodium hydroxide and blows the mixture of lead and fused alkali into a third chamber where the lead separates by its greater density and is returned to the electrolyzer. The fused caustic flows off continuously and is run into containers for shipment. The hydrogen

formed at the same time is permitted to burn. The steam performs not only the function of oxidizing the sodium but also circulates the lead. The working temperature of the cell is about 850° C. and the voltage 6–7; hence, although the current efficiency is fair, the power efficiency is low and the inability to produce strong gas is a disadvantage. This process was operated for some time at Niagara Falls but the plant was never rebuilt after it burned down.

*The Cylindrical Cell.* — In this type of cell the cathode, anode and diaphragm are assembled in the form of a vertical cylinder. The materials used in construction and operation are identical with, or similar to, those of other diaphragm cells, but the vertical cylindrical form offers certain advantages which have given this type of cell a very prominent place in industry and for this reason the development of this cell will be given in considerable detail.

*Development.* — The development of the cylindrical type of cell began at Wyandotte, Michigan, in 1904 at the plant of the Pennsylvania Salt Mfg. Co. This company had started producing electrolytic caustic using a mercury cathode cell patented by Geo. W. Bell. This cell proved a complete failure owing to the unsatisfactory manner of handling the mercury. The use of a diaphragm cell was suggested by Mr. A. E. Gibbs, of Niagara Falls, who brought out a small model of a cylindrical cell. The work of developing a commercial sized cell followed.[1]

*Details of Construction.* — The problem to be solved was to produce a cell of commercial size, which was placed at 1000 amperes, to be as simple as possible, and so constructed as to occupy small floor space, be easy to operate, and low in repair cost. Graphite was available for anode material and steel perforated cathodes had been found satisfactory. The circular form minimized the details of construction and permitted close grouping of the cells to economize space. The corrosion of the anode had to be guarded against.

*Anodes.* — In all rectangular cells until recently the anode was built up with joints in the carbon within the cell and this was a serious drawback as corrosion at the joints resulted and increased resistance ensued. This was to be avoided if possible. In the

[1] This early development is described in a paper published in Transactions American Institute of Chemical Engineers, Volume XVIII, part 1, 1920, by L. D. Vorce.

first large cell constructed this difficulty was not remedied, as the anode consisted of a large graphite cylinder with a plug screwed into the top for electrical connection. This not only introduced the undesirable joint but it also limited the size of the cell to the diameter of cylinder available. The capacity was also not as great as desired and this form was discarded.
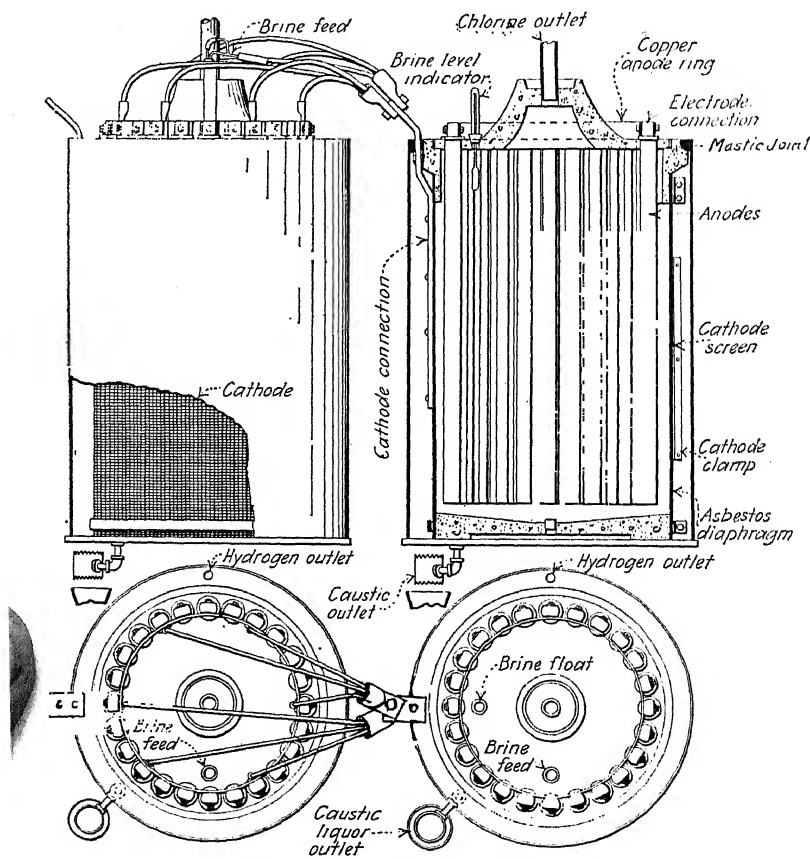


FIG. 141. Vorce Cell.

To avoid these features, recourse was had to a plurality of smaller pieces of graphite, and to secure the greatest surface exposure per volume of carbon, sticks $2 \times 2 \times 36$ inches were used. This gave two square inches of surface per cubic inch of

graphite, which was much greater surface exposure than in any other cell. It also permitted the use of twenty-four carbons in the anode in a circle of less than 22 inches (Fig. 141). Thus the current density at 1000 amperes would be considerably lower per square inch than in any of the other cells operating.

The cover or dome for supporting the carbon sticks, to withstand the action of the gas and chlorinated brine, was made of cast iron covered on the inside with hard rubber. The rings upon which the cathode pot was assembled were likewise of cast iron covered with hard rubber.

The machining of the ends of the carbon sticks to permit their being fastened in the cover was accomplished in a simple manner by means of a special cutting tool on the order of a spoke shave. Graphite may be threaded so that a locknut will make a closure capable of resisting the leakage of gas under normal conditions. This feature was unique in this cell. To prevent the creeping of the brine by capillarity up the carbon and corrosion at the electrical connection, the ends were impregnated with an oil to fill the pores.

*Electrical Connection.* — The carbons being now held securely, the manner of electrical connection was to be determined. Many devices were tried out in this connection before it was finally found that the best method was to bolt an annular strip of copper to each carbon head and attach as many flexible cables as needed to connect with the negative pole of the next cell in series. In this manner six cables, one for each four carbons was found to be satisfactory. These six cables constitute the so-called crowfoot and permit the rapid placing and connection of the cells without spending the time and care necessary to get proper alignment of cells where rigid copper bars are used.

The anode thus assembled is suspended in the cathode pot and supported in an annular recess provided for it in the top ring of the cathode pot. The two are then placed in the container tank which is of steel of suitable thickness.

Electrical connection was made to the cathode by means of four copper strips brazed to the top of the cathode sheet. The cathode sheet proper consisted of a steel plate having indented perforations with the rough burrs on the inside which served as additional support for the diaphragm. For the latter, asbestos paper alone was employed, as the use of cloth was found unnecessary. The cell as thus built and assembled is shown in

Fig. 142. The first of these cells was put in operation December 22, 1904.

*Feed.* — The brine was fed through the bottom ring of the cathode pot by means of a stuffing box arrangement which con-
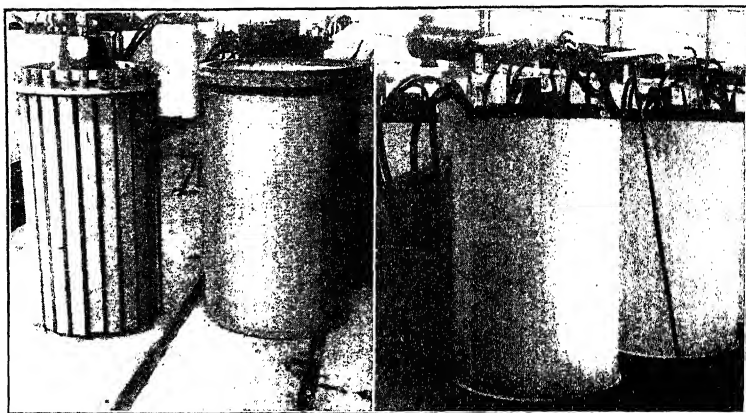


FIG. 142. Vorce Cell, Anode and Cathode.    FIG. 143. Vorce Cell Showing Gas Lines and Connections.

nected with the feed cup located on the side of the container by means of a rubber tube. This feed cup was adjustable for height to regulate the level of the brine in the cell.

The first feature which was noted as requiring modification was the elaborate stuffing box method of brine feed. Since at this time diaphragm cells were generally operated with unsubmerged cathodes, there was no considerable liquor head in the cathode compartment to be held back, so the bottom of the container tank was made with a fourteen inch center opening having a rim high enough to prevent the leakage of caustic and providing a seal for the hydrogen. With this change the brine inlet pipe could be fastened securely in the bottom ring of the cathode pot and connected with the feed cup by a rubber tube.

*Material for Cover.* — The next matter for development consisted of the three rings used, the dome or cover, and the two rings on which the cathode pot was assembled. The hard rubber covering for the cast iron rings could not stand continuous operation for any considerable length of time and in addition was expensive. A crack in the rubber was an invitation for immediate replacement and the junk value was negligible. The study of

available material for this purpose led to the development of a composition on the order of transite, which is a hard composition of cement and asbestos fiber, and the means whereby it could be formed into the shapes desired. It was comparatively easy to produce the bottom ring, which had all the physical appearance of a grindstone. After finding the great advantage of this substitute for hard rubber, the top ring of the cathode pot was perfected although presenting greater difficulty, and finally moulds were designed and built whereby it became easy to make all three rings. The cost was much less than one-half that of the rubber covered iron rings and the life several times as long. A proper impregnation with pitch reduced the corrosive action of the chlorinated brine and gas so that they last for years and resist leakage of the gas from the cell.

The depending neck of the top ring was made greater than it had been with the iron construction as an additional precaution against the passage of hydrogen into the anode compartment.

The cathode connection of brazed copper strips already mentioned was not satisfactory and was replaced by a heavy bar of copper capable of carrying the full current. It was securely riveted vertically on the side of the cathode opposite the vertical joint. This change also simplified the design and construction of the top ring.

*Current Leakage.* — In feeding a cell with a stream of brine of the amount needed in a 1000 ampere cell there is opportunity for current leakage back through the brine lines and also on the negative side in the caustic discharge. The positive leakage produces a certain amount of corrosion in the metal parts adjacent to the cell. While the power loss is not great it is very undesirable because iron is introduced into the cell and promptly deposits on the diaphragm to its ultimate destruction, as far as practical use is concerned.

A very effective cutoff of this leakage was worked out, which consisted in passing the incoming brine down through a column of petroleum oil held in a vertical glass tube. This gave not only a complete cutoff of the current but also served as a positive means of regulating the depth of the brine in the cell. Unfortunately it had to be discarded. It was impossible to prevent some of the oil passing over into the cells and becoming chlorinated, which not only tended to block the diaphragms but also passed into the gas lines and produced further complications.
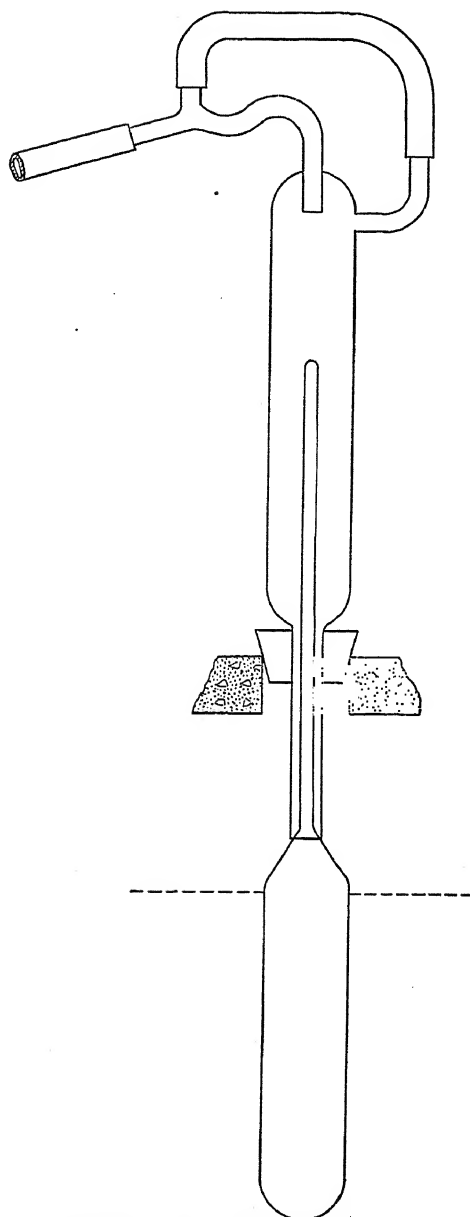
Fig. 144. Improved Brine Feed.

The ultimate relief came in a modification of a brine feed designed by Mr. D. A. Pritchard, which consists of a glass tube of an inch and a half diameter above the cell, with a smaller tube extending down into the gas space in which is a cutoff float which prevents the inlet of brine above a determined depth. The top of this tube is provided with a tee tube of special shape whereby the air above the brine in the large tube, under the pressure of the incoming brine, interrupts the incoming stream at the tee, so that it is fed in intermittent quantities. The broken stream cannot carry the current. For proper action the brine head supplying the cells must be carried at not too great pressure to overcome the upward pressure of the float.

*Special Tools.* — The production of a special form of apparatus, such as an electrolytic cell, calls for the design and construction of proper tools to facilitate the work of building and handling the cells, in

order to reduce the work to a minimum with its corresponding effect on the payroll.

These include the tools for trimming and threading the carbon sticks for insertion in the dome, the special tools for preparing the locknuts used for holding the carbons in place, the clamps used in applying the cathode, the design of drum used in rolling up the diaphragm paper, so constructed that it can be removed from the cathode pot after it is assembled as well as the special cast iron moulds in which the concrete rings are formed under pressure, etc. All this has tended to the production of a cell which has superceded to a large extent the older types of cell so that more of this type of cell have been installed than of any other type.
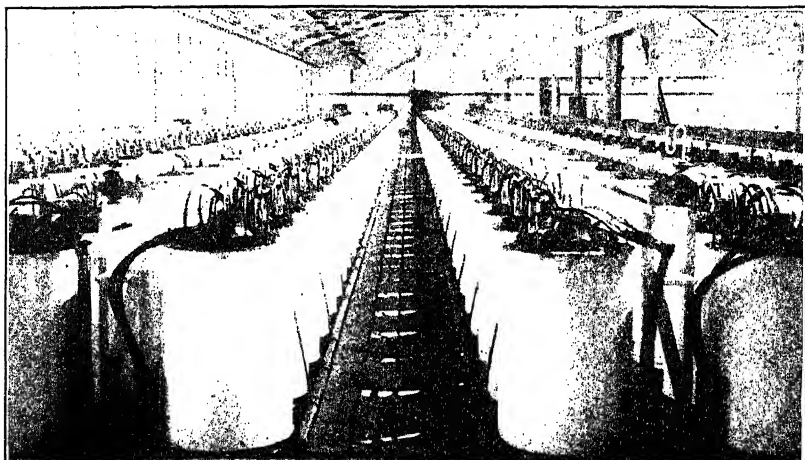


Fig 145. Electrolytic Caustic Soda Chlorine Plant.

*The operation* of an electrolytic caustic chlorine plant presents many problems demanding careful study. The success attained in running a cell plant is strictly proportional to the amount of attention to detail which is bestowed upon it. This does not mean that constant oversight of each cell is required, but it does mean that due care has been taken to invest the operation with all the precautionary measures required to produce the best results.

*The power* used must be substantially continuous and uniform. The ideal of the operator is to attain a continuity of current

approaching as nearly as possible to 8760 hours per year.    The reason is obvious.    When the current is off, the cells are not only non-productive, but they are in a measure self destructive for reasons explained earlier in this chapter.

*Purification of Brine.* — The brine used must be freed from all impurities which tend to impede the passage of the brine and current through the diaphragm or to destroy the anode or other parts of the cell.    No known deposit of salt is of sufficient purity to be used without some refining treatment.    Brine made from any commercial salt carries calcium and magnesium salts in varying quantities and these must be precipitated and removed to avoid clogging the diaphragm.    When the residual soluble sulfates are not in excess they may be allowed to remain.    If any considerable quantity is present its electrolysis along with the sodium chloride results in excessive oxidation of the anodes and an abnormal increase in the percentage of carbon dioxide in the chlorine.

*Life of Anodes.* — We have not yet reached the point where the anodes will last indefinitely.    Ordinary untreated graphite lasts from twelve to fifteen months.    Carbon impregnated with linseed oil to resist the oxidation lasts from eighteen months to three years depending upon the nature of the treatment, varying at different plants, and the conditions of operation.    A low current density with pure brine permits higher current and power efficiencies and longer anode life than a greater current impressed on the same cell.    There is no definite limitation in this respect. It resolves itself into a matter of economics.    A very high current may be in order when the maximum output is required in a limited space of time.

*The concentration of caustic* in the effluent is dependent on the amount of current and the porosity of the diaphragm, which latter is a function of its original thickness together with the degree of clogging to which it has been subjected.    Since the discharged caustic liquor carries an excess of undecomposed salt and must be evaporated for the concentration of the caustic and the coincident recovery of the salt, it will be evident that the price of fuel, determining the cost of steam, will have to be balanced against the cost of power, labor and repairs in operating the cells.    As already stated, a moderate current density works for higher cell efficiency.    It follows that with low priced power and high evaporating costs, the diaphragm should be adjusted

to deliver a maximum amount of caustic in the caustic effluent, thus reducing both the amount of evaporation and residual salt to be recovered. Thus, in localities where fuel is cheap, it is customary to operate with a caustic concentration of 7.5 to 9 per cent in the effluent. When freight rates increase the cost of the coal the caustic content is carried up to 10 to 15 per cent.

*Purity of Chlorine.* — The presence of $CO_2$ in the chlorine has been mentioned. The purity of gas leaving the cells depends on the density of the current, the purity and saturation of the brine, the construction of the cell to prevent gas leakage and the degree of suction applied in removing the gas as evolved at the anode. The purity of gas required naturally depends on its use. For liquefying and most chlorination operations, it should be as pure as is compatible with economical cell operation. With any well constructed cell the degree of suction on the gas collecting lines need be no greater than will hold an atmospheric pressure within the cell. A properly constructed cell, however, should withstand an internal pressure of at least an inch water pressure without leakage of the chlorine into the cell room and conversely should stand an inch or more of suction without contamination by air or hydrogen from the cathode compartment. The suction fan or pump should be controlled within these limits.

This presents the fundamental principles to be observed in conducting such an operation. The refinements cover a field much too copious to be treated in a chapter of this nature, and are in general to be acquired by practical application coupled with care and that rare trait, common sense.

**Evaporation and Marketing of Caustic.** — Depending on the cell used and the conditions under which it is operated, the operation of bringing the caustic to marketable condition will vary to a considerable extent. As shown in connection with the Acker cell, cells may be designed from which the caustic can be run directly from the cells into the steel drums which are used for shipping. In the mercury type of cells the caustic soda comes from the oxidizing chamber substantially free from salt and of a strength as high as, or higher than, 25 per cent NaOH. In all diaphragm cells, however, the effluent from the cathode compartment will carry a varying quantity of undecomposed salt and it may run from 7 or 8 per cent NaOH up to 12 or 15 per cent, with the salt from 16 to 17 per cent down.

*Evaporation of Caustic Liquor.* — It is customary to concentrate this cell liquor in vacuum pans or evaporators. Depending on the size of the plant and the amount of liquor to be handled per day, the work will be done in single, double or triple effect. As indicated in the chapter on evaporation this means that the heat from the steam used will be utilized once, twice or three times. Since the evaporation takes place under reduced pressure in vacuum pans, the boiling temperature of the liquid is substantially below what it would be at atmospheric pressure. As a consequence, low pressure steam can be used in the steam belt of the first pan. The steam vapor arising from the evaporation of the liquor in the first effect, passing into the steam belt of the second effect, boils the liquor in that pan in which a still greater vacuum is maintained. In dealing with a liquor of constant boiling point, several such passes may be utilized. With caustic salt solutions, in which the boiling point rises as the caustic strength increases, there is a definite limit to multiplying of effects.

The basis of the separation of salt is the fact that the salt is less soluble in the liquor than the caustic, so that as evaporation progresses, the salt crystallizes and falls to the bottom of the evaporator where it may be collected in so-called salt baskets, or the salt may be pumped from the bottom of the pans with some caustic liquor and the salt separated by suitable means. The caustic liquor is then returned to the evaporator for further concentration. Where multiple effect is used with low pressure steam, 3–5 pounds for heating the first effect, the concentration reaches a point where the boiling point of the caustic solution is so high that there is not sufficient difference in temperature between the steam in the heating belt and the boiling point of the solution to permit further concentration. Under these conditions the final evaporation to bring it to strong liquor takes place in a single effect evaporator which has a greater range in temperature between the incoming steam and the boiling point of the concentrating caustic.

*Continuous Evaporation.* — The evaporation may be carried out as a continuous process, that is, weak liquor enters one pan, losing part of its water and salt, and passes to the second evaporator in which it loses enough more so that it can pass continuously to the single effect finishing evaporator. In such a case the liquor entering the first pan, operating under a vacuum of

15–16 inches, will pass into the second effect at a density of from 15 to 20° Baumé and leave the second pan, in which 27–28 inches vacuum is being maintained, at a density of 35° Bé. Going then into the single effect, which is also under a high vacuum, it leaves that effect at 48 to 50° Bé., at which point it carries about 50 per cent NaOH with a small residue of salt.

At some plants the evaporation takes the form of a batch process, the liquor being retained in the pan until the desired concentration is secured, when the whole amount is pumped into the next effect, and in the second effect is treated in like manner, etc.

*Salt Removal.* — The strong caustic liquor from the single effect pan, carrying some salt in the hot solution, is passed through a cooling apparatus to crystallize out so far as possible the remaining salt, and, by settling or filtering, the salt still in solution can be reduced to about 17 grams per liter but cannot be further reduced by evaporation. As the caustic liquor at this stage weighs about 1500 grams per liter it contains 1.133 per cent salt, and when the residual 50 per cent of water is evaporated the percentage of salt in the solid caustic is proportionally increased but not enough to prevent the production of commercial 76 per cent caustic.

Where a grade of caustic calling for less than 2 per cent salt is demanded, it can be produced by a supplementary process. As is obvious from the nature of the evaporation and salt separation, the remaining salt exists in a saturated condition with respect to the solution. If the 50 per cent caustic solution be diluted to 40 per cent by addition of water, it renders the solution unsaturated with salt. By reducing the temperature of this solution a point is reached where the NaOH will crystallize out from the liquor, but the solution being unsaturated with salt it does not crystallize out. The caustic crystals can be filtered out practically free from salt and finished as solid caustic. The mother liquor is returned to the evaporating process. Much of the caustic now marketed goes out as strong caustic solution of from 54 to 50 per cent caustic content. It is shipped largely in tank cars or for smaller shipments in 55 or 110 gallon steel drums.

*Production of Solid Caustic.* — For solid caustic, the strong liquor is run into large cast-iron finishing pots which are ten feet in diameter and six feet deep. These are erected with furnace settings so that they may be heated with a free fire, coal, oil, or

gas. The cycle of operation of filling, evaporating, settling and pouring occupies about three days and a pot of the size mentioned will finish from 16 to 18 tons per charge. After the evaporation of all the water has taken place and the, caustic lies in a quiet molten state, a treatment with sulfur for removing iron, etc., is given it and, after settling, the molten caustic is either ladled, siphoned or pumped from the pot into the thin steel drums in which it solidifies and is then ready for shipment. Such drums are 21″ in diameter, made from 27 gauge steel sheets 34″ wide, and each holds from 730 to 750 pounds. The small opening in the top of the drum through which it is filled is closed with an iron cap to prevent moisture and dirt from entering.

**Handling the Chlorine Gas.** — Chlorine as it comes from the cells is saturated with moisture and very corrosive, so that it must be carried in stoneware, glass or rubber pipes until the moisture can be removed, after which it can be handled in iron pipe. The gas from the cells passes through a stoneware collecting line and thence through a series of pipes cooled by a water spray. For the removal of the moisture which the spray cooler leaves in the gas, it is conducted upward through a stoneware tower where it meets a downcoming flow of strong sulfuric acid. After this treatment the gas may be handled in iron or steel pipe without danger of corrosion.

*Bleaching Powder.* — Up to a few years ago all chlorine used for bleaching purposes was shipped in the form of bleaching powder. For the production of this material carefully hydrated lime is spread to a depth of four inches upon the floor of a tight chamger 20 by 100 feet built with lead or concrete walls, and so arranged that the chlorine gas can enter at one end and leave at the other. A number of such chambers are operated in series. To insure high test bleach in warm weather, the floor of the chambers must be cooled by refrigerating pipes imbedded therein through which cold brine circulates. The chlorine gas is absorbed in the slacked lime to the extent of 35–40 per cent, which is determined by withdrawing samples from time to time for test. When the sample withdrawn indicates that the chlorine content is sufficiently high, the gas within the chamber is pumped out into one with fresh lime and the finished bleach is dumped through holes in the floor of the chamber into casks or drums on a floor below. The work of packing bleach is disagreeable and hoods

for protecting the heads of the workmen are used, fresh air being continually supplied by a pump. The bleach package used is similar to that for caustic and holds 800 pounds.

As an improvement on the chamber system of making bleach, various mechanical devices have been used. The Hasenclever apparatus consists of a number of iron cylinders carrying mixing conveyors, placed one above the other. The hydrated lime enters at the top and works downward, meeting a counter current of chlorine gas which enters at the bottom. The chlorinated lime is discharged at the bottom into a hopper from which it is packed into drums.

Another modification consists of a long slowly revolving cylinder in which ribs on the cylinder serve to lift and drop the lime through the atmosphere of chlorine and carry it from the lime inlet end toward the gas inlet end and discharge it into a receiving hopper.

*Liquid Chlorine.* — Within the last few years the manner of shipping chlorine has undergone a complete change so that liquid chlorine has largely taken the place of bleaching powder. As chlorine condenses at 33° at atmospheric pressure it can be easily liquefied at a higher temperature under greater pressure. Hence all such operations combine refrigeration and pressure. If the pump which draws the gas from the cells and through the drying system can produce a pressure of from 20 to 40 pounds on the gas it may go at once into the brine cooled coils of steel, giving up its latent and sensible heat to the refrigerated brine and condensing to a heavy yellow liquid. While theoretically one pound of refrigeration will liquefy one pound of chlorine, in practice two pounds are used. In some operations the liquefaction proceeds in a double step. The dry gas from the towers is pumped to cooling coils at a pressure of 7 to 10 pounds where it is refrigerated to zero, but not below, before going to the pumps which compress it to 40 to 60 pounds. This step saves very materially in wear and tear on the compressor valves, etc. Since these compressors are lubricated with sulfuric acid steps to preserve them are needful.

*Non-Condensible Gases.* — In no case is the gas coming from the cells 100 per cent chlorine. Some carbon dioxide from oxidation of the graphite is present, together with air if cell tops and joints are not kept tight and, unless provided against, hydrogen may be present. To avoid the entrance of these

uncondensed gases into the storage tanks, a trap is arranged with a float valve which allows the liquid chlorine to flow into the receiver but holds the by-gas, or sniff gas as it is called, to be withdrawn from above and conducted away for the absorption of the residual chlorine which cannot be allowed to escape into the air.

*Shipment.* — Liquid chlorine is shipped in 100, 150 and 2000 pound cylinders and in tank cars holding from 15 to 30 tons. Receivers and tank cars are heat insulated, but one ton and smaller cylinders may be shipped without insulation. Most of the paper mills formerly purchasing bleaching powder have now changed to liquid chlorine from which they can make their own bleach liquors as required by absorbing the chlorine gas in milk of lime.

**Electrolytic Production of Aluminium.** — Metal aluminium is being produced on a very large scale by an electrolytic process in which a fused salt, cryolite, is used as the solvent for aluminium oxide which is decomposed by the electric current. Cryolite is a double fluoride of aluminium and sodium having the formula $AlF_3.3\,NaF$. A large deposit of this mineral found in Greenland is mined for use in the production of aluminium. . . .

Aluminium oxide dissolves in the molten cryolite to the extent of 20 per cent.

*Cell.* — The cell or "pot" as it is called is a rectangular box of heavy steel plate having an opening or tap hole for drawing off the molten aluminium. Soft steel bars are bolted to the side plates of the furnace shell and extend horizontally into the furnace a few inches above the steel bottom. These bars serve as current collectors. Electrical connection is made to the steel box which serves as the cathode. The steel box is lined with a mixture of carbonaceous material which is packed into the box and baked in place. The material used is ground coke blended with suitable amounts of tar and pitch. This material being very nearly pure carbon is a good conductor of electricity and serves as the cathode. The steel must not be allowed to come in contact with the molten aluminium which would dissolve some of the iron.

*Anode.* — The anodes are made of similar pure carbonaceous material mainly petroleum coke which is ash free. Any metal in the anode would be reduced and combine with the aluminium unless it were electronegative to that metal.

*The reaction* taking place during the electrolysis may be represented by the following equation:

$$Al_2O_3 + 3C = 2Al + 3CO.$$
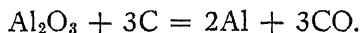
The primary reaction is undoubtedly the decomposition of the aluminium oxide, the aluminium being liberated on the furnace lining in a molten condition and accumulating on the bottom of the furnace. The oxygen in a nascent state is liberated at the anode reacting immediately with a hot carbon of the anode producing carbon monoxide and carbon dioxide. Theoretically the amount of carbon oxidized per pound of aluminium is two-thirds of a pound. In practical operations from ¾ to one pound of carbon will be consumed per pound of aluminium produced.

*Feed.* — The aluminium oxide from which aluminium is produced is the pure oxide made from bauxite. A charge is spread over the top of the molten cryolite where it is allowed to remain and become heated up. When the oxide in the bath has been decomposed, the resistance of the furnace rises sharply resulting in increased voltage to several times the normal value. The electrolyte no longer "wets" the anode which appears to be surrounded by a gaseous film through which the current forms arcs. At this point the aluminium oxide is stirred into the molten bath and conditions in the cell return to normal as the oxide dissolves in the electrolyte.

*Power Consumption.* — The voltage of the furnace under normal operating conditions is about 6 volts. The power consumption is 12.5 to 13 kilowatt hours per pound of aluminium, the theoretical power required being five kilowatt hours. The energy required to keep the bath molten as well as the melting of the aluminium oxide and the metal produced is furnished by the current as well as the energy for decomposition of the oxide.

The molten metal is tapped from the furnace from time to time when sufficient metal has accumulated.

REFERENCE

R. S. McBride. Modern Technology in Producing Pig Aluminium, Chem. & Met., **34,** 76–83.

PROBLEMS

63. Assume that 13 liters of saturated brine are fed per hour to a cell operating under 1,000 amperes and that the temperature within the cell is such that .2 per

cent chlorine goes into solution.  What is the maximum current efficiency which can be realized?

64. A concern operating a cell plant consisting of two series of 50 flat rectangular cells each at 3,000 amperes and 5 volts is producing caustic at 42.8 per cent power efficiency.  What is the current efficiency and what is the amount produced per hour?

65. The cells above occupy a room $60' \times 133' 4''$.  In this space six series of 72 cells of the cylindrical type could be installed to operate at 1,000 amperes and 3.5 volts.  Assuming the same current efficiency, what would be the production per hour and what would be the power efficiency?

66. In Problem 65, two motor generators of 3,000 amperes capacity at 250 volts feed one series each.  What rearrangement will be obvious to operate the six series?

# CHAPTER XIII

## SEPARATION OF SOLIDS AND LIQUIDS FROM GASES

P. E. LANDOLT, Chem.E.

The removal of solid or liquid particles from gases in industrial operations is an engineering problem requiring a thorough knowledge of gas engineering, together with an understanding of related plant operations.   In the solution of such gas cleaning problems and the design of the equipment it is essential to have a knowledge of the properties of gases and of the materials of construction necessary for the construction of suitable equipment.   The effects of corrosion and high temperature on such equipment are among the most important considerations.

Equipment for the separation of solid or liquid particles from gases, or gas cleaning apparatus, may be divided into two general classes:

(1) Dry Cleaners — for the removal of solids from gases.
(2) Wet Cleaners — for the removal of either solid or liquid particles from gases.

A further classification of methods may be made as follows:

1. Gravitational Methods.
2. Inertial Methods.
3. Filtration Methods (Resistance or obstruction to gas flow).
4. Spray Methods, which may also include 1 and 2.
5. Electrical Methods.

The degree or completeness of cleaning required to a very large extent determines the type of equipment to be selected. Plant operations also become a factor in the determination of what type of apparatus to use.   The first cost of the equipment as well as the cost of operation must be considered.

The information given in this chapter is presented primarily for the purpose of acquainting the student or plant engineer with

411

the types of equipment available and in use and also with some data on the fundamentals involved in the design of such apparatus.

**Nature of the Solid and Liquid Material to be Removed from Gases.** — Solids suspended in gases are either in the form of "dust" or "fume." Liquids are in the form of "spray," "mists" or "fumes." No sharp line of demarcation can be made to show exactly whether one term applies or not. The most important property of such suspended particles is that of size and weight. In general the above terms apply over certain ranges of particle size. Dust and spray are generally produced by strictly mechanical action, such as disintegration. Fume is generally produced by chemical action or volatilization. The size of fume particles at the time of their formation is probably molecular. Particle sizes have been carefully measured and the following list will give some indication of such sizes:

```
Talc dust........................9–10 microns
Silica dust......................3–5 microns
Ammonium chloride fume.........Approximately 1 micron
Paint pigments...................2–5 microns
Cement kiln dust
     Rock particles..............40 microns
     Fused coal ash..............5–10 microns
     Alkali fume.................1–5 microns
Carbon black...................Some particles smaller than 1 micron
Tobacco fume...................Less than 1 micron
Dust and spray particles.........75 to 3 microns or less
Fume particles.................Less than 3 microns
```

Another factor affecting the behavior of the suspended particles is their electrical charge. Experience has shown that this is usually a minor factor. The electrical charge of such particles however likely plays some part in the rate and extent of their agglomeration to facilitate their removal from the gases in which they are entrained. The charge on any given material may be either positive or negative.

**Fundamental Considerations.** — In gravitational methods, we are mainly concerned with the rate of settling of the particles. This is best expressed in Stokes law, which can be simply outlined as follows:

(1) $$V = \frac{gd^2\rho}{k\nu} = \text{velocity of fall},$$

$d = $ diameter of particle,

$\rho = $ density of particle,

$g = $ acceleration due to gravity,

$\nu = $ viscosity of the gases,

$k = $ a constant.

The rate of fall of particles in still air would be as follows:

```
d.............................Settling rate
Microns......................Ft. per sec.
100..........................3
74...........................1.6
10...........................0.03
1............................0.003
```

Stokes law applies also to inertial methods in the following form:

(2) $$V = \frac{d^2\rho\gamma\omega^2}{k\nu},$$

where $\omega$ is the angular velocity of the gas and

$\gamma = $ radius of curvature of the gas path,

$k = $ a constant.

Other factors as in the first equation.

This equation may be reduced as follows in a circular path at uniform velocity:

(3) $$V = \frac{kD\nu}{S\rho d^2},$$

$V = $ uniform velocity,

$S = $ angular distance through the apparatus.

In cyclone apparatus, therefore,

```
d.............................Gas velocity
Microns......................Ft. per sec.
100..........................8
74...........................15
10...........................800
1............................80000
```

At gas velocities below 10 feet per second gravitational or settling methods are to be preferred but at velocities above 10 feet per second, inertial methods become important.

If we take equations (1) and (3) above we can demonstrate the importance of this statement from equation (1):

$$(4) \qquad D = k_2 \frac{gL}{V},$$

where

$L$ = length of settling chamber,
$D$ = distance particle is moved out of the gas stream,
$k_2$ = constant = $d^2\rho/k\nu$.

From equation (3)

$$(5) \qquad D = k_2 VS,$$

where

$V$ = uniform velocity,
$S$ = angular distance through the apparatus,
$k_2$ = constant $k_2$ in equation (4).

At a velocity of 3 feet per second, with a settling chamber 10 feet long, $D$ equals approximately 107 $k_2$.

At a velocity of 3 feet per second in a baffled chamber where the gas passes in a complete half circle at such length as to equal the time of passage through the 10 foot settling chamber, $D$ equals approximately $9k_2$.

For 10 feet per second velocity

$$D = 32k_2 \text{ (gravitational)},$$
$$D = 30k_2 \text{ (inertial)}.$$

At 20 feet per second velocity

$$D = 16k_2 \text{ (gravitational)},$$
$$D = 60k_2 \text{ (inertial)}.$$

In filtration methods, we are mainly concerned with having a filtering medium with sufficiently small interstices through which the gas may pass with a reasonable pressure drop and on which the suspended matter is retained.

The filtering medium must be resistant to attack by the gas as well as the suspended matter accumulated on it. As the accu-

mulation of material increases on the filtering medium, the resistance to gas flow increases and provision must be made for removing such material continuously or periodically.

With dry filtration methods, temperature and humidity of the gases must be maintained within rather close limits.

Mists are sometimes filtered but in such cases the filtering medium acts as an agglomerator causing the mist particles to coalesce into drops which are then easily removed from the gases.

In a spray tower, the particle size of the spray medium should be regulated in accordance with the size of the suspended matter. A coarse spray would be generally effective in removing dust, while a fine spray might be necessary for the removal of a fume. Here, however, condensation effects by cooling action of the spray must be taken into consideration.

In filtration methods, high velocities of gas mean excessive power costs.  In spray methods a high gas velocity tends to carry the spray medium along with the gases and then additional equipment of a gravitational, inertial or other kind must be provided to complete the gas cleaning operation.[1]

**Classification of Gas Cleaning Apparatus.** — Table I gives a list of many of the types of equipment in commercial use.  This table is presented to give a quick reference for each apparatus and following the table is given some description of each type of equipment.

**Gravitational Collectors.** — *Settling chambers* have been and are still used in smelting plants, iron blast furnace plants, cement mills and other operations.  Frequently such chambers are simply long large flue sections, as much as a mile in length with the gases passing through them at a velocity of 1–20 feet per second.

*Howard Dust Catchers* were developed by Mr. Henry Howard for dust recovery from pyrites roaster gases for sulfuric acid manufacture.

The diagram (Fig. 146) indicates its general construction and size for a furnace roasting approximately 15 tons pyrites per 24 hours.  The gas capacity of the apparatus is approximately 4000 c.f.m. @ 1000° F.  Its efficiency of dust removal is 60–90 per cent

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[1] Anderson, Trans. Am. In. Chem. Eng., Vol. XVI, 1925.

TABLE I. — General Classification of Gas Cleaning Apparatus

| Limit of Use | Temperature | Dry | Type of Equipment | Wet | Principal Use |
|---|---|---|---|---|---|
| | | | *Gravitational* | | |
| Corrosion......... | Construction materials. | X | Settling chambers............. | | Coarse dust cleaning |
| | Construction materials. | X | Howard Dust Catchers......... | | Pyrites burners — $H_2SO_4$ mfg. |
| Destroyed by acid gases | Construction materials. | X | Wire dust catchers (Roesing, etc.)... | | Smelting plants — Settling flues |
| | | | *Inertial* | | *Dust Problems* |
| | Limit for steel work... | X | By-Products Recoveries, Inc. ...... | | Dust problems |
| | Limit for steel work... | X | Dust Recoveries, Inc. — Vorticose.. | | Dust problems |
| | Limit for steel work... | X | Cyclone collectors............. | | Dust problems |
| | Limit for steel work... | X | Sirocco-Vortex (Davidson Cyclone).. | | Dust problems |
| | | | Murray Washer............ | X | Cinder catcher |
| | Limit for steel work... | X | Centrifix Corporation........... | | Dust problems |
| | | | Doherty Washer............. | X | Tar extraction |
| | Limit for steel work... | X | Multiclone................. | | |
| | | | *Resistance or Obstruction* | | |
| | | | *To gas flow (inc. filters)* | | |
| | | | *Bag Filters* | | |
| For non-corrosive material and gases | 200°–250° F......... | X | Halberger-Beth System (German)... | | Dense insulating fume and miscellaneous limited volume cleaning problems (under 50,000 c.f.m.) |
| | 200°–250° F......... | X | Allis Chalmers............. | | |
| | 200°–250° F......... | X | Dust Recovery & Conveying Co..... | | |
| | 200°–250° F......... | X | Holly Bag Filters............ | | |
| | | X | Northern Blower Company........ | | |
| | | X | Stocking dust collectors......... | | |
| | | | *Screen Cloth Collectors* | | |
| | | X | Sly Dust Arrester............ | | Packing machines — Cement, flour, etc. |
| | | X | J. W. Paxson Company......... | | |
| | | X | Pangborn Dust Arrester......... | | |
| | | X | New Haven Sand Blast Co...... | | |

Table I. — *Continued*

| Limit of Use | Temperature | Dry | Type of Equipment | Wet | Principal Use |
|---|---|---|---|---|---|
| Corrosion | Atmospheric | X | Gravitational<br>Mid West Steel Co. (Film cleaners) | | Air cleaning for turbo-generators, etc. |
| | On reducing gases only on temperature up to 600° F. | X | Kling-Weidlein Cleaner | | Iron blast furnace gas cleaning |
| | Below 100° F. | | P. & A. Tar Extractor | X | Tar extraction |
| | 200°–250° F. | | Calder Fox Scrubber | X | $H_2SO_4$ mist removal |
| | Below 100° F. | | Smith Glass Wool Filter | X | Tar extraction |
| | | | Mineral wool and asbestos filters | X | $SO_2$ gas cleaning for $H_2SO_4$ mfg. |
| | | | *Spray Methods* | | |
| | Below 150° F. | | Feld Washer (Bartlett-Hayward) | X | Secondary cleaning iron b. f. gas for gas engines, etc. |
| | Atmospheric | | Theissen Washer | X | |
| | | | Theissen Disintegrator | X | |
| | | | Steinbart, Bassert and Zschocke Towers | X | Primary iron b. f. cleaning for stores and boilers |
| | | | Carrier Engineering Co. | X | Air cleaning (conditioning) |
| | | | *Electrical Methods* | | |
| | Limit of construction materials | | Steere Tar Agglomerator | X | Tar extraction |
| | | | *Electrical Precipitation* | | |
| | | X | Cottrell | X | See Table III |
| | | X | Lurgi (Cottrell-Moeller) | X | |
| | | X | Lodge — Cottrell | X | |

depending on the fineness of the dust recovered.    It is usually shut down once a month for cleaning.

*Wire Dust Catchers.* — Dust chambers hung with wires have also been used in smelting practice for many years.    The deterioration and replacement of the large quantities of such "wire" baffles constituted one of the serious objections to this method.
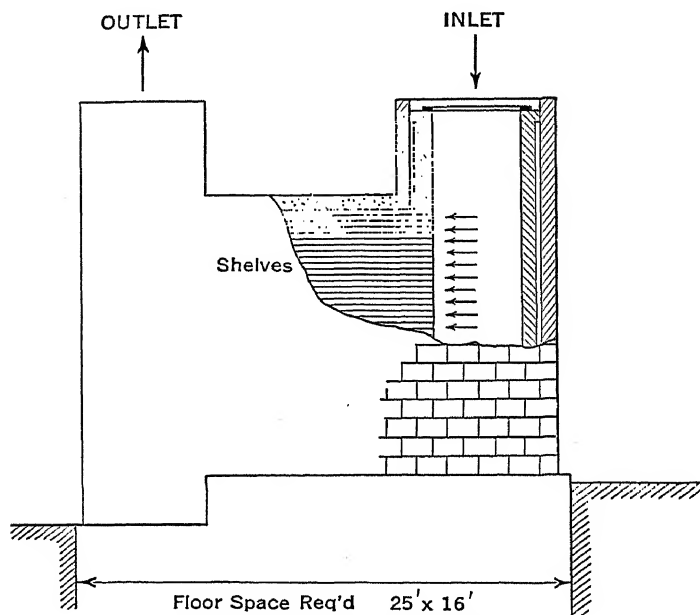


FIG. 146.    Howard Dust Catcher.

**Inertial Collectors.** — *Cyclone Collectors.* — In the operation of cyclone collectors or "arresters," gases enter the side of a vertical cylinder, the inside of which is so designed as to give a centrifugal motion to the gases when they enter the apparatus at a given velocity — usually 2000 to 3000 feet per minute (Fig. 147).

The cleaned gases are discharged from the center of the top of the apparatus. The dust collected falls into a hopper and is discharged.    This type of apparatus is most effective on relatively coarse dust particles (above 15 microns) and on a relatively great concentration of such dust particles (10 grains or more per cubic foot of gas).    The back pressure developed in such apparatus usually varies from 2 to 3 inches of water.

In practice the efficiency of dust recovery varies between 50 per cent and 95 per cent. Usually with an average of approximately 70 per cent. Smaller size units are ordinarily more effective than large units. For example, small units—0.25–5.0 sq. ft. inlet area, handle up to 10,000 c.f.m.; large units — 20–50 sq. ft. inlet area, handle up to 120,000 c.f.m.

*By-Products Recoveries, Inc.* — In this apparatus (Fig. 148) the velocity of the gases is alternatively increased and decreased through nozzles, the direction of gas flow being reversed in each cycle. The apparatus consists of a steel box containing a series of metallic nozzles, screens, and boxes so arranged that the gases impinge on the screens or perforated plates at a high velocity. The dust is carried through the screen and drops into a dead gas space and thence to a dust hopper.

The gases pass through a group of such nozzles and screens in series adequate for the cleaning of the gas and within the limits of reasonable pressure drop — usually 1–1½ inches of water. There are usually 10–14 "boxes" in series. These
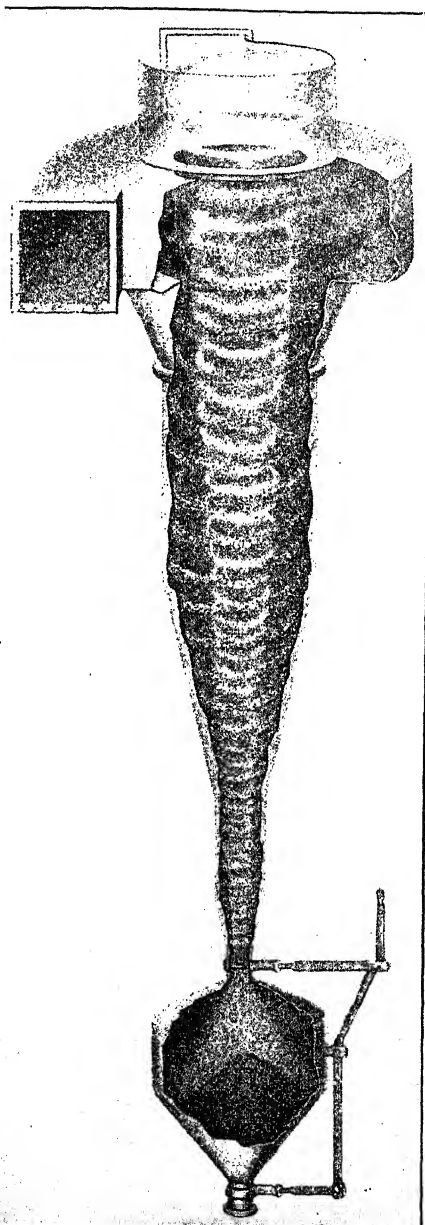


Fig. 147.   Sirocco-Vortex Collector.

boxes are mechanically shaken periodically to remove the collected dust and prevent clogging.
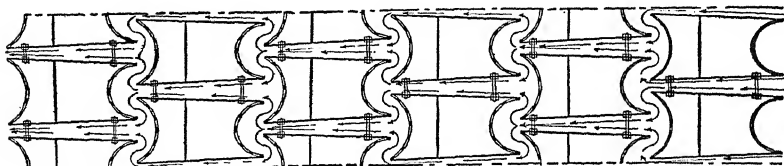


FIG. 148. Diagrammatic Plan View of Gas Movement through Machine.
(By Products Recoveries, Inc.)

*Dust Recoveries, Inc.* (*Vorticose*). — This apparatus consists of series of staggered baffles against which the gases impinge and ange direction, dropping their suspended dust into dust ppers (Fig. 149).
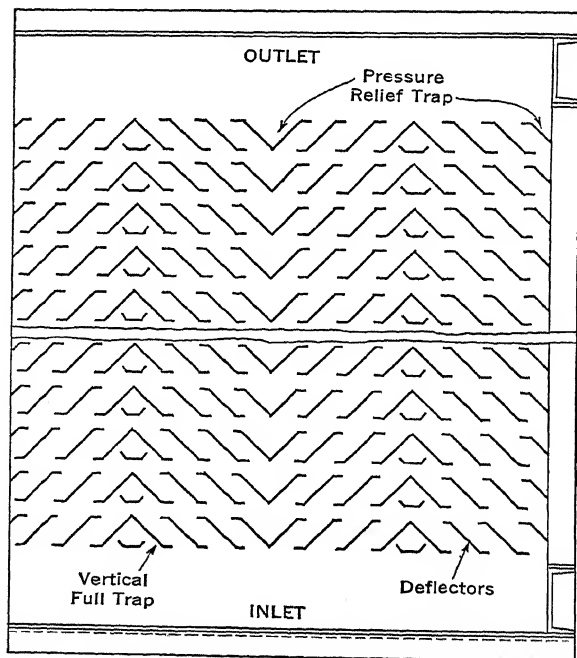


FIG. 149. Vorticose Collector, Plan View.

**Automatic Bag Filters.** — In this type of cleaner, the gases are passed into long tubular bags on the inner surface of which the dust or fume collects and the cleaned gas passes into an outer chamber and through mechanically controlled valves to the discharge flue. The mechanism that controls the valves also operates a shaking system to clean the dust- or fume-laden bags. The apparatus is arranged in units of usually 16 bags each, the bags being usually 8″ to 10″ diameter by 12 to 20 feet long. During the cleaning periods the gas flow is reversed, returning the gas to the inlet connection as some of the material removed from the bags during cleaning may be carried along with the gases (Fig. 150 and Fig. 151).
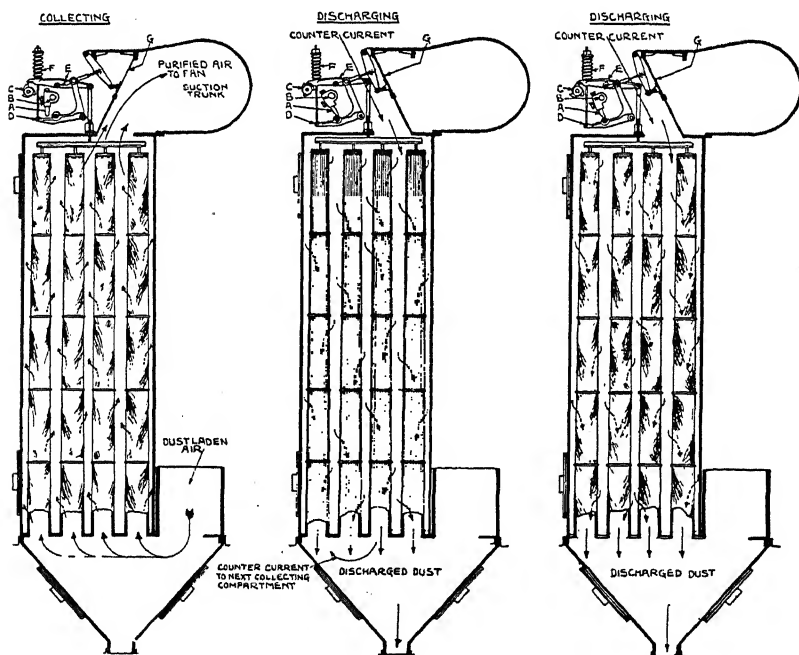


Fig. 159.   Dust Collector.   (Automatic Bag Type.)

This type of cleaner is limited by the following conditions:

1. *Temperature* at which the bags lose strength.   For cotton cloth this is at or below 210° F., for wool 250–270° F.

2. *Corrosion* — excessively caustic materials or acid gases impair or destroy the bag fibre.

3. *Moisture* — any condensation of moisture clogs the bags and interfere with their proper cleaning.

4. The pressure drop across such an apparatus is three to six inches of water.

The small "stocking" collector consisting of a number of bags which are rotated and automatically cleaned, is mainly useful in connection with air cleaning in certain manufacturing operations; such as food products, drugs, etc.
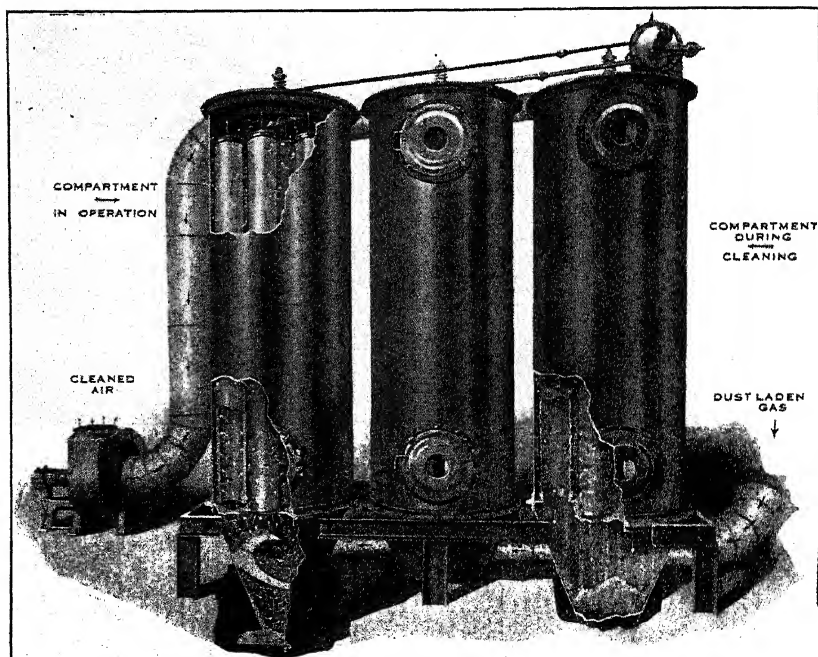


FIG. 151.   Perfecto Filter.   (Dust Recovery & Conveying Co.)

**Screen Cloth Collectors.** — Screen cloth collectors usually consist of a series of screen cloths placed vertically in a rectangular metal box through which the gases must pass.   The screens are arranged in zigzag fashion to give maximum filtering area.

The dirty gas enters the "dust chamber" in which the gases lose their velocity and some of their dust.   After passing through

the screens, the cleaned gases enter the clean gas chamber beyond which is placed a suction fan to draw the gases through the chamber and overcome the resistance of the screens. The screens are periodically shaken to preserve the collected dust. The screens are usually shaken mechanically. If the gases contain a large quantity of moisture, the moisture may condense and clog the screens. The pressure drop through the apparatus is 3 to 6 inches of water.

*Kling-Weidlein Cleaner.* — This cleaner consists of a mat of special steel wool mounted on shelves with the gases usually passing up through the mats for cleaning. The chamber in which these mats are assembled is usually heat insulated. At regular intervals the mats are mechanically shaken, the dust falling down into a hopper at the bottom.

This apparatus has been applied to the dry hot cleaning of iron blast furnace gas. It operates with an appreciable pressure drop owing to the resistance of the mats. Iron blast furnace gas has been cleaned in this apparatus to less than 0.40 grain dust, per cubic foot of gas at 62° F. and 30″ Hg, remaining in the gases.

*Mid West Air Filters.* — For air cleaning, a film cleaner had been developed in Germany and later exploited in the United States by the Mid West Air Filters, Inc. Relatively large masses of a solid, usually cast iron, are placed in a frame and the surfaces of these solid pieces are coated with a grease or heavy oil. As the air passes through these frames, the dust particles in it are retained on the film of grease or oil. The frames are renewed periodically, the grease melted off, the dust separated, and the cleaned grease recovered for future use. A multiple unit of the frames is assembled to handle the required amount of air. It is obvious that this type of filter can be considered only when a small amount of dust or dirt is contained in the gas (Fig. 152).

*P. & A. Tar Extractor.* — This equipment was originally developed in France and consists of a series of concentric perforated plates through which the gases pass. The perforated plate baffles tend to "squeeze out" the tar particles. This apparatus removes about 75 per cent of the tar contained in manufactured gas. The pressure drop across this apparatus is one to two inches of water.

*Calder-Fox Scrubber.* — This scrubber was designed at the Chance and Hunt Company, Ltd., in England for the removal of sulfuric acid mist from concentrator gases. It consists of two or

three perforated lead plates in series, so perforated as to give the gases a sharp change of direction in a very short length.    The perforations are usually about 1/64″ diameter and the space between the plates is approximately 1/8″.    Over 90 per cent of the acid mist can be removed in this apparatus but the pressure drop is 6 to 10 inches of water.    The gas velocity through the orifices or perforations is approximately 100 feet per second.
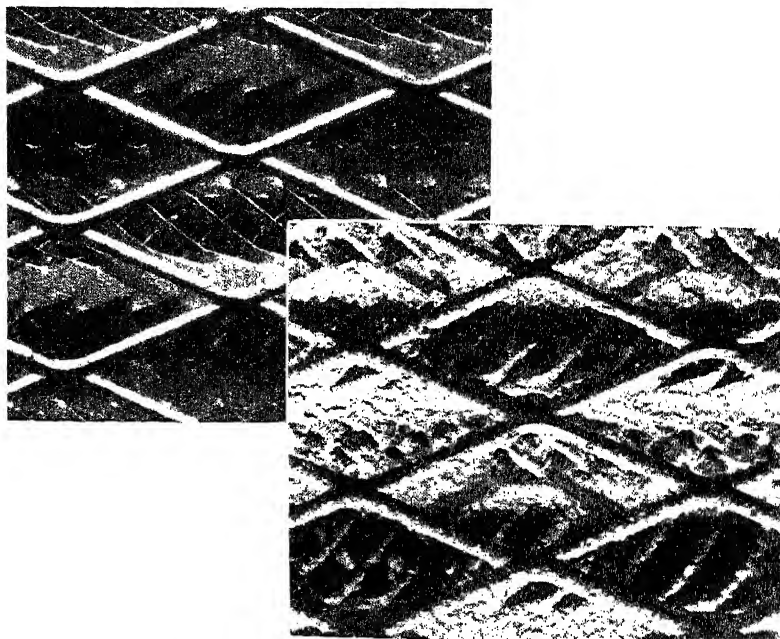


Fig. 152.    Photograph of Clean Range Filter and Same After Several Weeks' Service.    Must be Cleaned before Further Use.

*Glass Wool Filter.* — In this equipment the gases pass through a diaphragm or filter of glass wool.    This apparatus was developed to clean cooled producer gas.

Asbestos, mineral wool, coke, anthracite coal, sand and stone as filtering media have been widely used in chemical plants for gas cleaning.

**Spray Methods.** — *Murray Washer.* — The Murray Washer (Fig. 153) was developed for the removal of relatively large

particles of cinders from boiler house stack gases.   These boilers were stoker-fired and operated under heavy draft.

It depends for its operation on the impingement of a high velocity jet on a wet surface, usually a bath of water.   The gases are turned through 180° in their passage over the water surface.
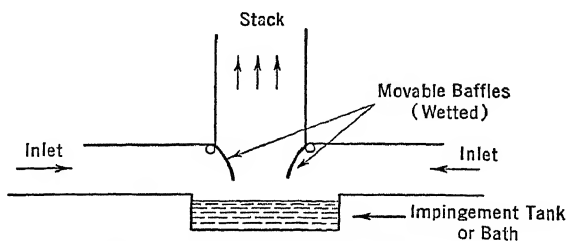


Fig. 153.   Murray Washer Diagram.

For the conditions for which this washer was designed, it is effective in removing cinder particles.   Efficiency of removal of suspended matter of such character is over 90 per cent.

It is limited in its use due to its interference with draft at heavy load periods and due to corrosion from heat and by sulfur compounds.

*Feld Washer.* — The Feld type washer, originally developed in Germany, depends for its operation on the principle that dust particles by contact with large surfaces or films of water are "screened out."   The gases pass through a series of such "water screens" and the dust-bearing water is deposited by the centrifugal action of a central impeller (Fig. 154).

A number of washing chambers are placed one above the other.   A vertical shaft rotates a set of arms which spray the water through an ascending column of gas by means of five solid shells and an outer perforated shell shaped like the frustrum of a cone.   A thorough mixing of the gases and water takes place and a high degree of cleaning is obtained (Fig. 155).

*Doherty Washer.* — This washer consists of a steel box with a series of vertical baffles.   The gases pass over and under these baffles alternately.   It is used principally as a rough cleaner for the removal of tar and for the cooling of gases in gas works.

*Theisen Washer and Disintegrator.* — The Theisen Washer (later the Disintegrator) was developed in Germany for the secondary cleaning of iron blast furnace gas for use in gas engines and heating operations.

ADJUSTABLE OVERFLOW

LIQUID

GAS

GAS
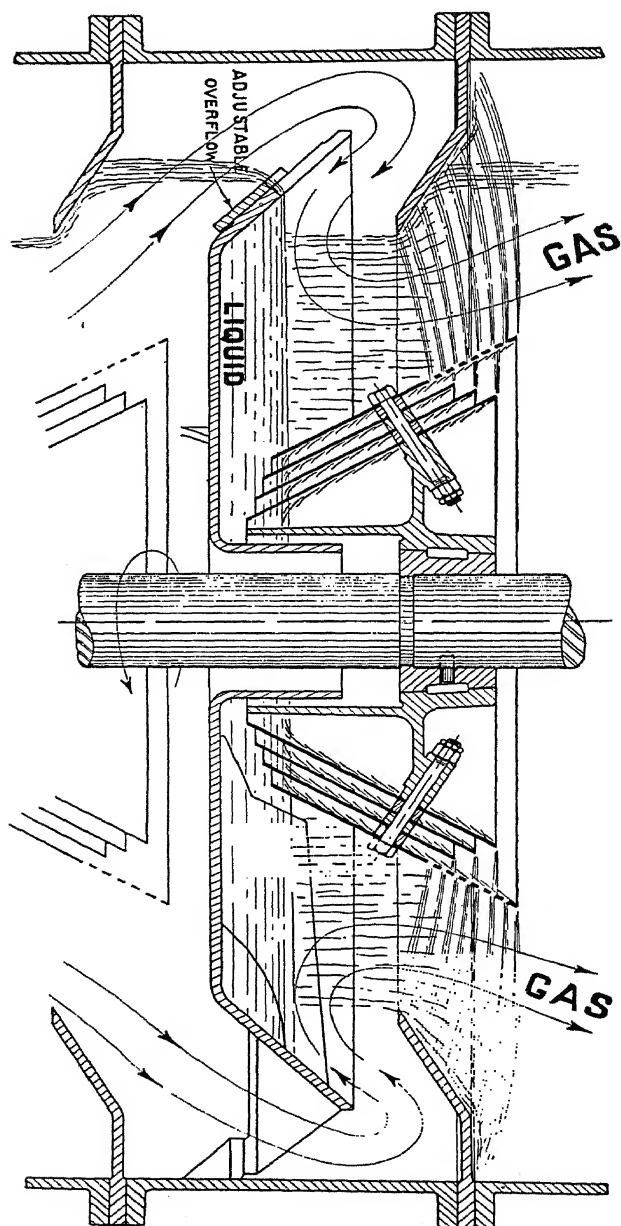
FIG. 154.   Sectional View of Feld Washer.
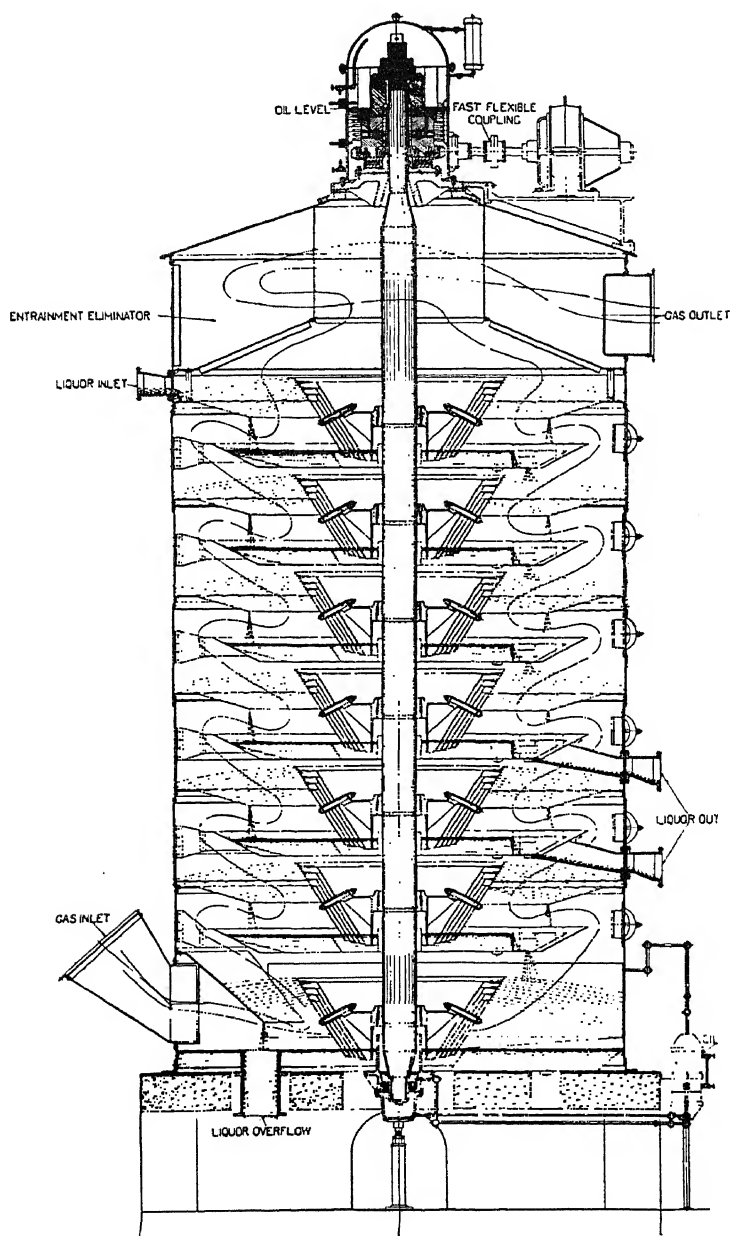
FIG. 155.   Typical General Arrangement of B. H. Co. Scrubber (Feld Type).

The Theisen machine consists of a rotary element rotated at a speed of 300–450 r.p.m. which whirls the gases and wash water in relatively thin films so that very intimate contact is brought about between the two fluids. This results in a thorough "rinsing" action which cleans the gases to 0.02–0.005 grains/ft³., at 62° F. and 30″ Hg. The power consumption is very high, about 350 H.P. for 35,000 c.f.m., at 62° F. and 30″ Hg.

*Tower Washers.* — Tower washers have been widely used in the chemical industry. These towers may be packed with quartz, coke, or other suitable material or with spiral or annular stoneware rings or plates or bricks. Water or other scrubbing liquid is fed to the top of the tower and flows down through the tower, contacting with and scrubbing the ascending gases. Sometimes to prevent clogging, open towers are used and sprays form a "rain" in the tower which gives adequate wet surfaces for the washing of the gases.

Wash towers may also serve as cooling and reaction towers, as in the manufacture of sulfuric acid.

The steel industry also has used tower washers for the primary cleaning of iron blast furnace gas. The principal towers designed for the cleaning of iron blast furnace gas are the Zschocke, Steinbart, Brassert and McKee Washers.

**Electrical Methods.** — There are two methodes of electrical gas cleaning: agglomeration and precipitation. In both cases it is necessary to pass the gases through an intense electric field in which the gases are "ionized" or charged and as a result, the suspended particles are either agglomerated or precipitated.

*Agglomeration.* — In electrical agglomeration, the gases are passed between two electrodes, one charged with a high voltage alternating current, the other being grounded. The gases ionized by the action of the electric field furnish the means of charging or ionizing the suspended particles both positively and negatively, so that particles oppositely charged are attracted and then agglomerate or coalesce into larger particles which can then be removed by other methods.

In electrical precipitation, the gases are also passed between two electrodes, but in this case the charged electrode is charged by a unidirectional current at high potential and the suspended particles are removed from the gases while they are passing between the electrodes or through the resultant electric field.

In electrical precipitation, a number of unique features may be observed.

It is not limited by particle size as are the gravitational and inertial methods.  It is not limited by resistance to gas flow as are the filters or scrubber type apparatus.  Its resistance to gas flow is negligible.  It is also not limited by close ranges of temperature as are, for example, cloth filters.  It is also easily adapted to the cleaning of very large volumes of gases with a consequent reduction in unit cost as compared with other types of equipment in which unit size is more or less fixed and must be multiplied in proportion to the quantity of gas cleaned in a given time.

The function of the electrical precipitation apparatus known as the "precipitator" is three-fold: It provides the electric force or field, it charges or ionizes the particles and it removes them from the moving gas stream.

The degree of completeness with which the gas particles are ionized determines to a large extent the completeness of removal of the suspended particles.

The velocity of a gaseous ion in a precipitator may be 100 feet per second or more.  The separating velocity would be less than 1 foot per second.

Assuming a fume concentration of 30 grains per cubic foot (much above normal) and assuming the fume to be made up of single particles of 1 micron diameter and density of 2.5, there would be 10,000 ions present for each fume particle.

The ionization of the suspended particles must depend on the chance of the particle getting in the path of the gaseous ions. This chance is greater for a larger number of particles exposed to a gas ion stream.

It can therefore be demonstrated that if gases containing suspended matter pass through a precipitator at a velocity "$V$" and if "$P$" is the proportion or fraction of the initial amount of suspended matter which is ionized and precipitated at this velocity, the following relation will approximately hold:

$$1 - P = K^{1/v}.$$

| $P$ | $V$ (feet/second) | $K \times 10$ (calc.) |
|---|---|---|
| 74% | 26.1 | 55 |
| 80 | 21.4 | 56 |
| 87 | 17.4 | 54 |
| 93.4 | 12.9 | 54 |
| 95 | 11.4 | 55 |
| 98 | 8.6 | 59 |

These data are based on actual field observations on mist particles. The character of the mist and the electric force impressed on the apparatus were kept constant.

It is evident that the values of "$K$" remain practically constant, increasing somewhat as the removal of suspended matter approaches 100 per cent.

The value of the constant "$K$" varies with the electrical field strength, the type of precipitator and the nature and size of the suspended matter (Fig. 156).



Curve 1 3—Calculated
  "  2  —Observed

$\frac{1}{V}$    $V$  Velocity—Ft. per Sec.

Curve 1    $K = 30$
  "  2    $K = 55$
  "  3    $K = 70$
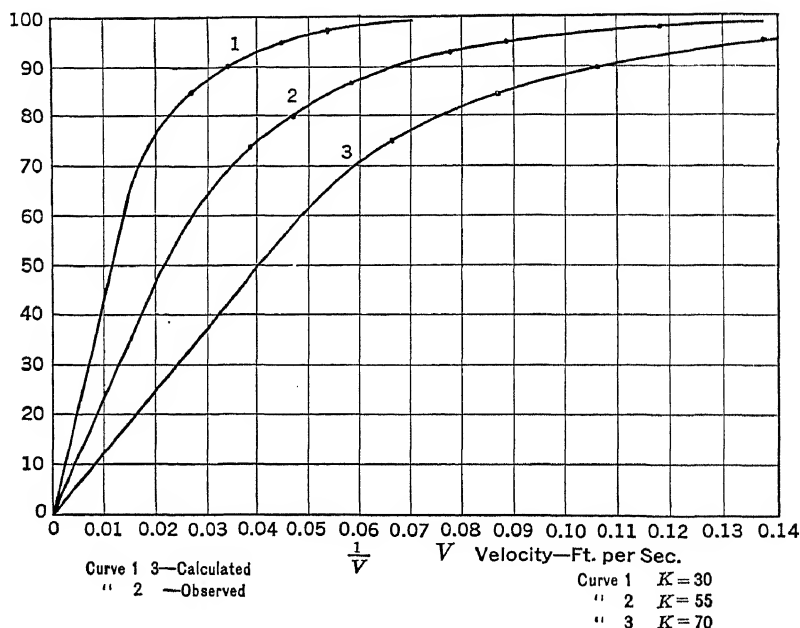
FIG. 156.  Efficiency-Capacity Rating Curves.  (Cottrell Process.)

For further details and original work on the fundamentals of gas cleaning, reference may be made to the following:

*Cottrell Precipitation Process.* — Removal of suspended matter from gases by electrical means is accomplished through the use of an intense electric field. An electrically charged particle in an electric field tends to move toward the positive pole or electrode if its charge is negative and toward the negative pole if its charge is positive. The suspended particles receive their charge from

charged or "ionized" gases with which they are in contact and also by induction if the gases are passed through an electric field.

Gases are ionized by intense heat, cathode rays, radium emanations, or other means. In electrical precipitation, advantage is taken of the fact that an intense electric field, indicated by the presence of a "corona" discharge, will ionize gases, and if a unidirectional current is used to produce the electric field, then charges of one kind will be produced, charging the suspended matter identically, which is then repelled from the source of the charge of the same kind, which is the charging electrode.

To bring this about, the charged electrode is made of a more or less filamentary element, having a surface with a large radius of curvature. The receiving electrode has an extended surface and is grounded. The suspended matter is driven from the charged electrode to the grounded electrode where it loses its charge and "collects" on the extended surface.

The simplest combination of electrodes is a fine wire for the charged electrode placed axially in a smooth pipe for the grounded electrode. Best results are obtained when the charged electrode is negative, due possibly to the higher velocity of negative ions.

The principal investigators in this field, who first placed the aforesaid theories into practice, have been Sir Oliver Lodge in England, Dr. Frederick G. Cottrell in the United States and Erwin Moeller in Germany.

Two groups of equipment are essential to carry out this process: electrical equipment to generate the high potential unidirectional current required to produce the intense electric field; and the precipitation chamber in which the gases are cleaned or "treated."

For practical use of the process, the high potential current must be produced from standard electric power circuits. Usually 220, 440 or 550 volt alternating current, either 25, 50, or 60 cycles, is used, either 1, 2 or 3 phase. Where only direct current is available, a motor generator set must be used to produce low voltage alternating current.

*Equipment Required.* — Low voltage alternating current is transformed to a voltage of 30,000 to 75,000 volts, and is then rectified by a synchronously driven mechanical rectifier or other rectifying unit. The mercury arc rectifier was used by Lodge. The "Kenetron" or high vacuum tube rectifier has also been used. Other means of rectification have been suggested or tried.

Accessory equipment is used to control the special requirements of the operation (Figs. 157 and 158).
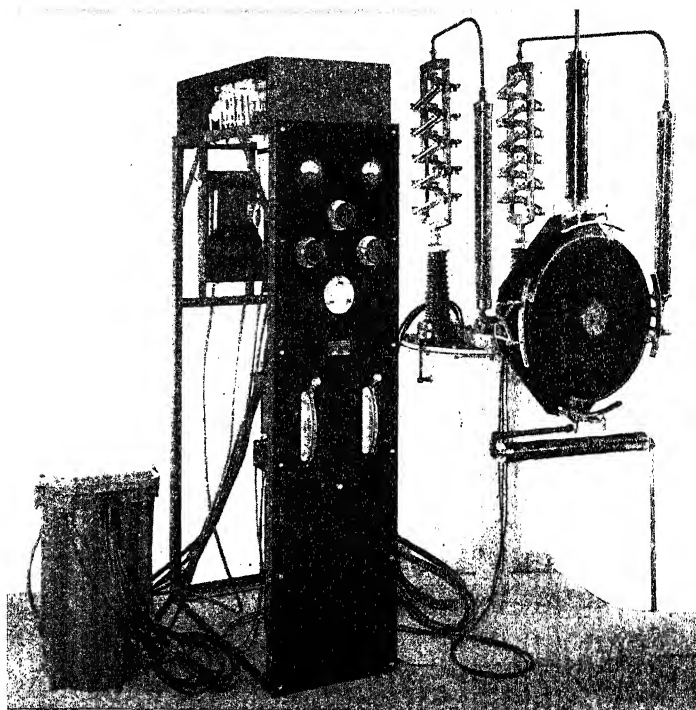


Fɪɢ. 157.   Complete Set-up of 15 K-Va. Cottrell Electrical Set with Accessory Equipment.

*Precipitator.* — The precipitator or chamber in which the gas cleaning is accomplished is usually of the "pipe type" or "plate type." The pipe type consists of a number of pipes or tubes, either round or square, 6″ to 12″ diameter by 9 to 15 feet long. The pipes are placed vertically between upper and lower header chambers and in each pipe a charged electrode is hung axially and insulated from the main structure. The gases pass up or down through the pipes for cleaning. The pipes are arranged for mechanical cleaning or rapping when dust or fume is collected in them. In some cases the pipes are arranged for flushing the collected material from their surfaces.

The plate type consists of a series of plates hung perpendicular to the gas flow with the face of the plate parallel to the gas flow. Charged electrodes are hung mid-way between plates from insulated frame works.
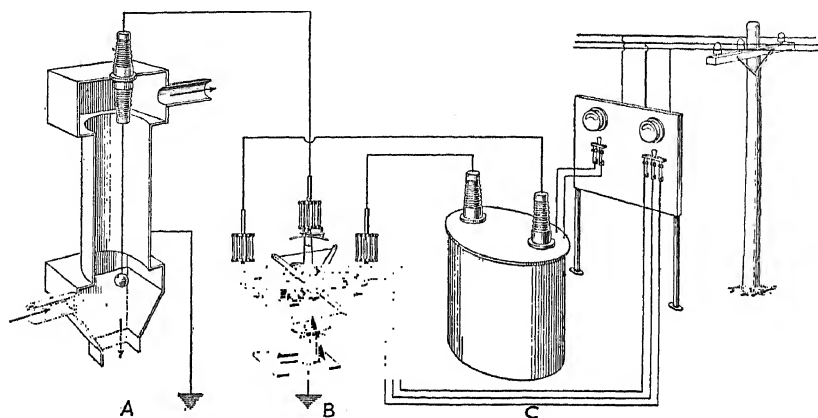


FIG. 158.   Diagrammatic Cottrell Layout.

Plates take the form of corrugated iron sheets, screens with baffles, rods, or semi-insulating material (cement) with conducting rods imbedded in them (Fig. 159).

Plate precipitators are usually arranged for horizontal flow of gases and may have from one to five plate sections in series.

*Practical Considerations.* — The size of the precipitator is largely determined by the volume of the gases to be treated per unit of time, the velocity of the gases through the apparatus, and the properties of the material which is to be removed from the gases. Temperature and composition of the gases also have some bearing on the design of the precipitator and the capacity required to obtain a desired efficiency of removal of the suspended matter.

Having determined the size of precipitator required, the number of units and capacity of the electrical equipment can then be determined.

Cottrell installations may be designed for any pre-determined efficiency, in some cases as low as 75 and as high as 99.9 per cent.

Draft or pressure loss through precipitators is usually negligible, but, including pressure loss through the inlet and outlet

Direction of
Gas Flow

**CORRUGATED PLATE**

Gas Flow

**ROD CURTAIN**

Gas Flow

**GRADED RESISTANCE**
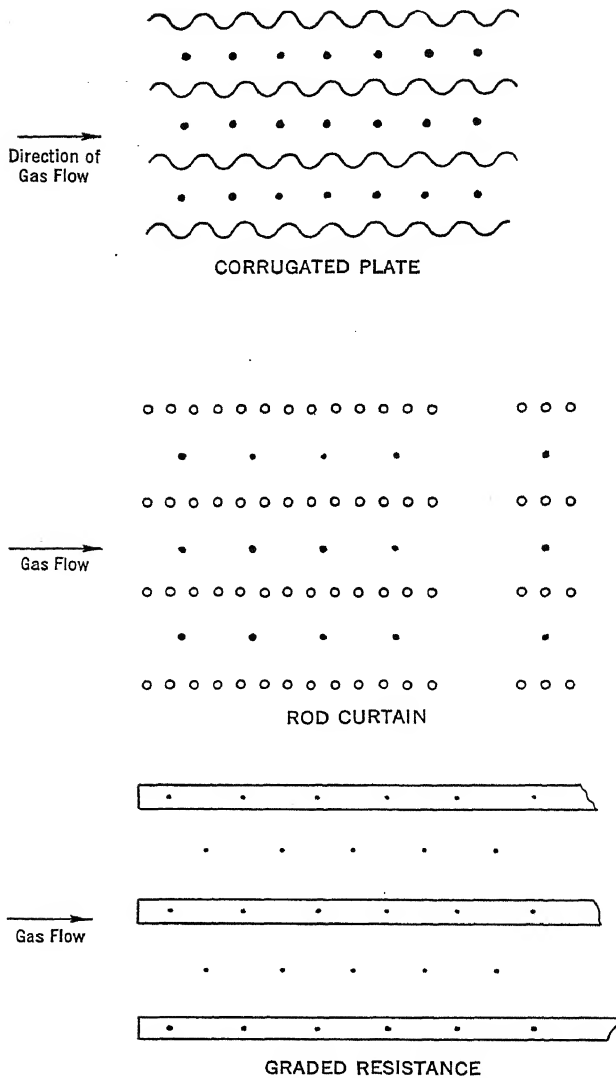
FIG. 159. Plan Diagram—Plate Precipitator.

flue connections, the total pressure drop is usually less than 0.5 inch of water.

Cottrell apparatus has been designed and is operating at temperatures up to 1200–1300° F.  If necessary, the apparatus can be heat insulated so that the temperature drop through it does
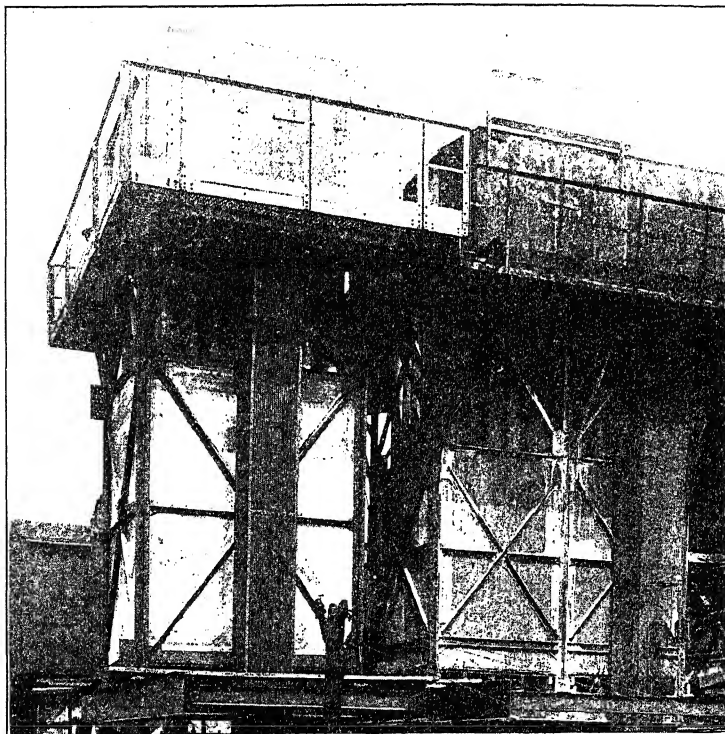


Fɪɢ. 160.  Sulphuric Acid Mist Precipitator (Sludge Acid Concentration).

not exceed 100° F., at an inlet temperature of 1200° F.  Cottrell equipment operates continuously.  Provision is usually made for by-passing individual precipitator units, particularly in large installations, for cleaning and repairs.

The following table gives some cost figures of representative installations in North America.

TABLE II. — COTTRELL PROCESS — TYPICAL COST DATA

| | (Dust) Copper Roaster Gases | H₂SO₄ Mist Concentrators | H₂SO₄ Mist (SO₂ Cleaning) | (Dust) Boiler House Gases (Powdered Fuel) | (Dust) SO₂ Gases Hot | Detarring of Gases | Cement Kilns (Dust and Fume) |
|---|---|---|---|---|---|---|---|
| Approximate investment per rated cubic foot per minute and treatment conditions... | $0.80–$2.00 | $2.50–$4.00 | $4.00–$5.00 | $0.30–$0.40 | $1.50–$2.00 | $1.50–$2.00 | $0.60 |
| Temperature of gases treated — °F... | 600–700 | 200–300 | 70–100 | 300–400 | 1000–1200 | 90–120 | 250–800 |
| Cleaning cost per 100,000 cu. ft./hr... | $0.05 | $0.15–$0.18 | $0.25–$0.35 | $0.01–$0.02 | $0.15–$0.20 | $0.06–$0.15 | $0.02 |
| Power consumption K.W. hrs./100,000 cu. ft... | 0.5 | 0.8–1.00 | 0.8–1.0 | 0.3–0.5 | 0.4–0.5 | 0.5–0.8 | 0.25 |
| Efficiency of removal of suspended matter, per cent... | 95 | 96+ | 99.9 | 90 | 95+ | 95–98 | 95+ |
| Relative electric field size based on H₂SO₄ mist equal to 100 per 100,000 cu. ft./hr... | 200 | 100 | 130 | 150 | 240 | 86 | 150 |
| Spacing — Plate to plate (or pipe diameter... | 8″ | 8″–10″ dia. | 8″ dia. | 8″ | 8″ | 6″ dia. | 6″–8″ |

**Summary.** — In general for gas cleaning problems, the data essential to a proper consideration of the problem and the selection and design of suitable apparatus are as follows:

(1) Volume of gases to be treated per unit of time.
(2) Temperature of the gases, with a chart showing maximum, minimum and usual working average.
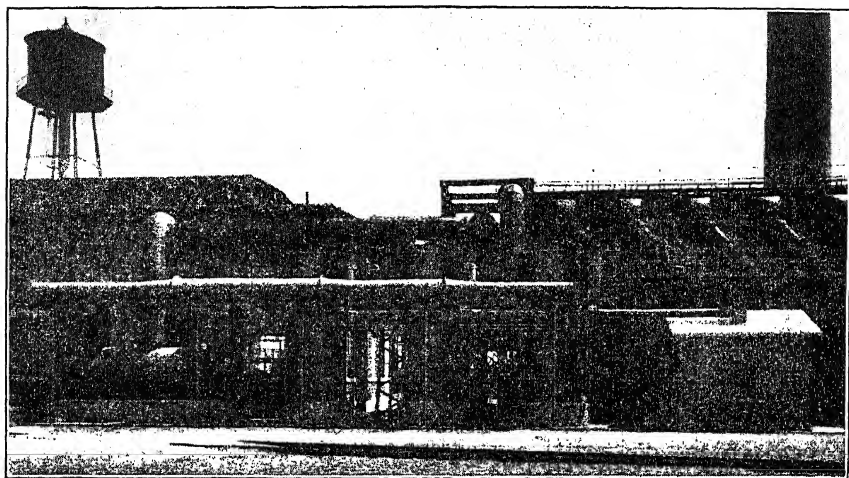


Fig. 161.   Detarring of Coke Oven Gas.   (Cottrell Equipment.)

(3) Pressure of the gases, with information on related operations and the effect of resistance to gas flow on such operations: furnaces, ventilation equipment, fans, flues, stacks, etc.
(4) Humidity of the gases — relative humidity of gases below 212° F., water content in grains per cubic foot in gases above 212° F.
(5) Gas composition — particularly acid constituents.
(6) Quantity of suspended matter per cubic foot of gas.
(7) Physical and chemical properties of the suspended matter.
(8) Degree of cleanness required (efficiency).
(9) Availability of electric power and water.
(10) Utilization of cleaned gases and recovery of by-products from the suspended matter.
(11) Operating costs and maintenance.
(12) Available space for the equipment.
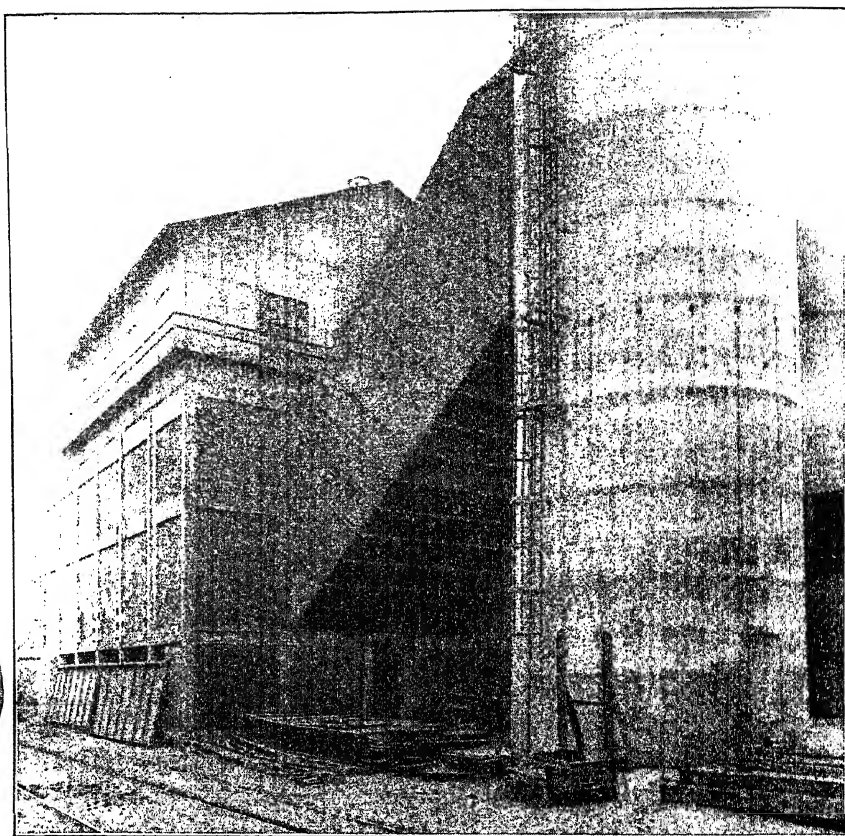
FIG. 162.    Cottrell Dust Collector on Cement Kiln Gases.

The following table gives a classified list of the commercial applications of the Cottrell Electrical Precipitation Process.

TABLE III. — COMMERCIAL USES OF ELECTRICAL PRECIPITATION

1. Non-ferrous metallurgical dust and fume.
    *a. Materials recovered:* compounds of copper, lead, tin, zinc, silver, gold, platinum, bismuth, arsenic and others.
    *b. Operations:* dryers, roasters, sintering machines, blast furnaces, reverberatory furnaces, converters and others.
2. Acid problems.
    *a.* Sulfuric acid: concentrators for new, spent and sludge acid.
    *b.* Nitric acid — nitrating operations.
    *c.* Hydrochloric acid — roasting operations, pickling.
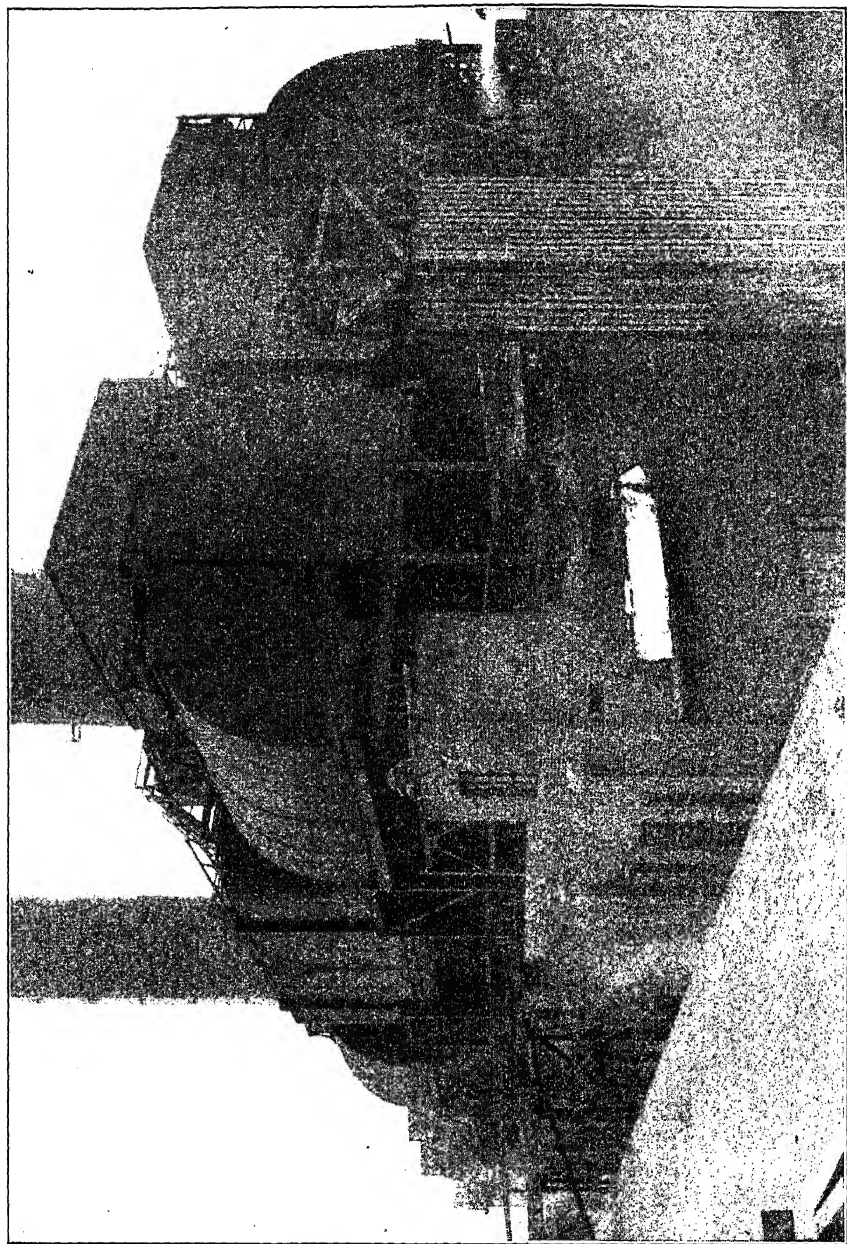
Fig. 163.   Cottrell Dust Collector on Powdered Fuel Fired Boilers.

    *d.* Phosphoric acid, phosphate rocks reduction in both electric and fuel fired furnaces.

    *e.* Miscellaneous, chlorine and bromine recovery.

3. Smoke, soot, cinder.

    *a.* Boiler plant gases — powdered coal fired.

    *b.* Engine round houses.

    *c.* Lamp black from oil — carbon black from natural gas.

4. Gases containing sulfur dioxide.

    *a.* Hot gases — pyrites and blende roaster gases for sulfuric acid manufacture.

    *b.* Cold gases — for contact acid manufacture; for sulfite liquor production.

5. Combustible gas cleaning.

    *a.* Iron blast furnace gas cleaning. Primary — hot stoves and boilers; secondary — for gas engines and heating processes.

    *b.* Hot producer gas cleaning — dust removal.

    *c.* Tar recovery from producer gas, illuminating gas, coke oven gas, low temperature distillation, wood distillation.

6. Air cleaning.

    *a.* Small capacity installations — foundries, machine rooms, etc.

    *b.* Large volume installations — slate crushing.

7. Miscellaneous applications.

    *a.* Portland cement manufacture — kilns (wet and dry operations), dryers, grinders, crushers, tube mill vents, etc.

    *b.* By-product potash recovery from cement kiln gases or otherwise.

    *c.* Large electric furnace fume recovery.

    *d.* Dust and fume from miscellaneous chemical plant operations.

    *e.* Organic materials — from spray drying and other operations.

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### PROBLEMS

67. A cement mill using the wet process produces 5000 barrels of clinker per day. The fuel consumption is 120 pounds of coal per barrel, coal containing 8 per cent

ash.   The raw material consists of limestone and slag, and the slurry contains 34 per cent $H_2O$.   Waste heat boilers are used to cool the gases.   Gases at the mouth of the kiln contain 24 per cent $CO_2$ and beyond the kiln the dilution of the gases is 80 per cent.   Gas temperature beyond the waste heat boilers and economizers is 350° F.

1. Calculate gas volume to be treated beyond the waste heat boilers.
2. Where would be the best location for the dust collector?
3. What type collector should be used?   For high efficiency?   For 50–60 per cent dust recovery?
4. What disposition of cleaned or partially cleaned gases?
5. After selecting suitable type dust collector, determine size and ground space required.   Make sketch of layout.

68. In a plant using multiple hearth roasters, 50 tons of Spanish pyrites are roasted daily.   Ore contains 48 per cent sulfur and is roasted to 2 per cent sulfur. The roaster gases leave the roaster at 1400° F., containing 7 per cent $SO_2$ by volume. The gases are cleaned and then cooled and purified, and then oxidized catalytically to $SO_3$ to form sulfuric acid.

1. Calculate volume of gases formed at 1200° F.   100° F.
2. What type equipment should be used to clean the hot gases to remove dust carried over the roasters?   To remove same almost completely?   To remove 60 per cent to 75 per cent?
3. What equipment to purify the cooled gases to remove suspended acid mist or dust or fume or both?
4. Make sketch layouts of equipment, giving approximate sizes and location relative to roaster furnaces and acid plant equipment.

69. In a stack 15'0'' internal diameter having gases containing dust concentration of 1 pound per 1000 cubic feet, describe where and how the station for measuring total gas volume passing up the stack and for determining the concentration of suspended matter should be located.   Prepare log sheet of necessary observations including gas temperature, static pressure, meteorological data, velocity pressure.   Describe instruments used for making gas measurements and also describe the gas sampling equipment used.

# CHAPTER

## MATERIALS OF CC

JOHN C. OLSEN, Ph.D., D.Sc.

**Importance of Corrosion.** — The selection of the most suitable materials for the construction of chemical apparatus and equipment is one of the most important duties of the chemical engineer. As chemical operations usually involve the use of acids, alkalies, and other highly corrosive substances, chemical apparatus may be quickly destroyed unless constructed of highly resistant materials. Chemical operations are frequently carried out at high temperatures at which corrosive action is greatly accelerated. At times, operations are carried out under pressure which may range from a few pounds to several tons per sq. in. so that great tensile strength is required. The severest conditions involve the use of corrosive chemicals at high pressures and temperatures. Failure of the apparatus under these conditions may involve not only loss of the material and apparatus, but also injury and possible loss of life to workmen or operatives. Corrosion may not only limit the life of the apparatus but may also contaminate the material being produced. In many cases a given operation cannot be carried out because the material for the construction of the necessary apparatus is not available. Development of a process often resolves itself into the problem of development of the material for the construction of the apparatus in which to carry out the process. An illustration of this is the development of chemical stoneware which rendered possible the production of muriatic acid and other acid materials. It has been found necessary to develop methods for the production of acid resistant enamel-lined apparatus in order to be able to manufacture certain chemicals and food products in a high state of purity, as in some cases very small amounts of metallic impurities render chemicals valueless.

**Effects of Corrosion.** — Resistance to corrosion by the acids, alkalies or other corrosive agents so commonly used in chemical

operations is probably the most essential and common require-
ment for materials of construction of chemical equipment.  In
some cases an impurity introduced from the apparatus in one
stage of a process may be taken out in a subsequent operation.
For instance, if the apparatus is constructed of iron and a reaction
involving the use of acid is carried out, some iron will go into
solution, but if in the next step the solution is made alkaline, the
iron may be precipitated and can be filtered off.   If the amount
of iron dissolved is not excessive, it may be cheaper to use ap-
paratus constructed of iron and replace it occasionally rather
than to employ a more expensive material.   Under such con-
ditions the apparatus may be made extra thick or heavy in order
to prolong its life.   If the rate of corrosion is known, the approx-
imate life of the apparatus can be easily estimated.   Corrosion
data are frequently given in fractions of inches penetration per
month in order to make estimation of life of the equipment
convenient.

It is also possible at times to modify a given process so as to
reduce the corrosive effect.   It may even be desirable to discard
a process and devise a new method for producing a given product
so that a less expensive equipment or material may be used.   In
developing commercial processes it is very necessary to keep in
mind the character of the equipment which will be required to
carry it out on a factory scale.

**Rate of Corrosion.** — In making a study of the resistance to
corrosion of materials of construction, the concentration and
temperature of acids and corrosive agents must be considered,
as well as the effect of the presence of other chemicals.   Oxidizing
agents, and even the presence of the oxygen of the air, frequently
exerts a marked influence on corrosion.   In studying the effect
of chemicals on test pieces the size of the piece should be noted
so that the area exposed may be known.   It is generally most
convenient to weigh the test piece before and after immersing it
for a definite time.   The loss in weight should then be calculated
to thickness of the material dissolved in a definite time, so that
the length of life of a given piece of equipment of known thickness
can be calculated.   This can readily be done by dividing the
loss in weight by the density.   If the corrosion is not uniform
but pitting is noticed, the maximum penetration must be taken

as the depth of corrosion in order to estimate correctly the serviceable life of the material.

**Prevention of Corrosion.** — It is possible very greatly to reduce the amount of corrosion, or at times entirely prevent it, if the conditions producing corrosion are understood. The electrolytic theory of corrosion has been generally accepted as best accounting for the observed facts. According to this theory corrosion may be represented by an ionic reaction of the following type:

$$M + \overset{+}{H} = \overset{+}{M} + H.$$
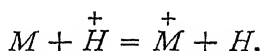
$M$ represents an atom of the metal being acted upon which goes into solution as a positive ion while a hydrogen ion from the solution gives up its charge to the metal and is deposited as a hydrogen atom. When a layer of hydrogen atoms or molecules has formed on the surface of the metal the atoms of the metal can no longer pass into solution as ions and the action ceases unless the layer of hydrogen is removed. This may take place by bubbles of hydrogen leaving the surface or by oxidation of the hydrogen layer. The presence of an oxidizing agent in the solution or dissolved molecular oxygen from the air will accomplish this result and serve to accelerate the corrosion. Rapid motion of the liquid also accelerates corrosion.

While most cases of corrosion are due to the presence of acid ions in the solution, hydroxyl ions will also cause corrosion.

**Corrosion of Metals.** — Corrosion proceeds much more rapidly if two metals are present and in contact with each other, forming an electrolytic couple. The more positive metal goes into solution while the more negative metal is protected from corrosion. Similar action takes place if a compound is formed on the surface of the metal which is electronegative to the metal. This is true of iron rust which tends to accelerate the corrosion of metallic iron. On the other hand, in some cases a protective coat may be developed which will protect the metal from further corrosion. Aluminum is protected against the action of acids by a coat of oxide or basic compound. At some concentrations of sulfuric acid a coat of sulfate of lead is formed which protects lead from further corrosion. A high concentration of sulfuric

acid will dissolve this coat of lead sulfate exposing the lead to continued corrosion.

Other conditions being equal, corrosion increases with the temperature, the logarithm of the corrosion rate being inversely proportional to the absolute temperature, the equation being as follows:

$$\log R = A + \frac{B}{T},$$

$R$ being the corrosion rate, $T$ the absolute temperature and $A$ and $B$ constants.   For many homogeneous reactions the velocity of corrosion is doubled for each 10° rise in temperature.

**Corrosion Tests.** — While a large amount of corrosion data has been published, and the resistance to corrosion of the standard materials is known in a general way, it is frequently desirable to carry out corrosion tests with the exact solutions to be used, keeping the temperature, velocity of the liquid, and other conditions identical with that to be used in the process.   In this way the life of the equipment may be accurately estimated.

**Selection of Materials.** — A list of some of the more important materials used for the manufacture of chemical engineering apparatus is given in this chapter with some of their most important properties and the apparatus for the construction of which they have been used.   Where a material has already been used for a given operation, experience has accumulated showing its fitness and limitations for that specific operation.   When selection must be made of a material for a new piece of apparatus or operation this experience is available and is often of very great value.   The selection should be made by listing the requirements of the process in the order of importance or, still better, by the preparation of a list of the requirements in which the importance of each property is suitably weighted.   The most important requirements are then taken care of first.

For instance, for an autoclave, strength of material is of primary importance.   From the tensile strength of the material to be used the thickness of the walls, bolts, etc., may be calculated, making due allowance for a liberal factor of safety.   If corrosion takes place, the rate of penetration is ascertained by experiment, additional thickness of material being added and the life of the

apparatus estimated.   Replacement may be necessary in a few months or a longer period.   The cost of the apparatus may then be computed per pound of product on the basis of the amount of material which can be produced during the life of the apparatus.

In some cases it is more economical to utilize a cheaper material even though it must be replaced oftener.   The ratio between the service life of the apparatus and the initial cost plus the cost of repair or replacement and the shut-down charges less the scrap value of the material, will give the true cost index of the apparatus. Very often processes become obsolete within a few years and are re-placed by more economical processes developed by research. Equipment need not be designed to last longer than the probable life of the processes, particularly when the longer life is due to the use of more expensive material.

*Coated Materials.* — In some cases, it is possible to produce a satisfactory apparatus by a combination of two or more materials, taking advantage of the special properties of each material.   For instance, tanks for the storage and shipment of muriatic and other acids have been constructed of steel having a lining of hard or soft rubber.   The steel gives the requisite strength to the container while the rubber lining acts as a protective coating, not being acted upon by the acid.   Among the metals, lead has been found to exhibit excellent resistance to corrosion but unfor-tunately this metal has very little mechanical strength.   In many cases excellent apparatus can be constructed by using lead as a lining and securing the requisite mechanical strength from other materials such as wood and steel.   Processes have been developed by which lead has been permanently bonded to steel for the production of a great variety of chemical equipment.

Some materials, such as glass, while having excellent resistance to chemical action and considerable mechanical strength, are very sensitive to shock or change of temperature and are therefore fragile and not suited for practical use.

*New materials* having useful properties are being continually developed and put upon the market.   Manufacturers' claims for these products are not always substantiated by experience.   On the other hand, in many cases only the manufacturer of chemical apparatus has sufficient knowledge of the properties of a given material and the experience in its fabrication to judge as to the best size, shape and details of design of apparatus constructed of a given material.

Success in the use of chemical apparatus often depends upon proper construction of the apparatus. The advice of an experienced and reliable manufacturer must often be sought before deciding upon the use of a given material. This is given by the technical service department of the manufacturer.

### Iron and Steel

The various forms of iron constitute the most largely used metal in the chemical industries. As fabricated into wrought and cast iron and steel, this metal possesses an extraordinarily wide range of properties. Taken in connection with the low cost and availability, its extensive use is readily understood.

The purest commercial form of iron, namely: wrought iron, is a tough, highly ductile metal which is admirably adapted for the manufacture of piping which can be bent into any desired form. The high carbon, high silicon, metal known as cast iron has great rigidity and compressive strength and can be readily cast into a great variety of apparatus such as kettles, autoclaves, pipes, etc. By varying the percentage of carbon in a highly refined iron, steel may be produced having a very wide range of tensile strength and toughness. Apparatus requiring very high tensile strength such as autoclaves and bombs are constructed of steel. By the addition of various alloying metals such as vanadium, chromium, nickel, molybdenum, etc., the tensile strength can be very greatly increased and in some cases very high resistance to chemical action will result.

**Corrosion of Iron.** — The greatest defect in most forms of iron is the ease with which it is attacked by dilute acids and oxidizing agents, including the oxygen of the air. Enormous quantities of ferrous metals are destroyed annually by these two agents. The metal is very highly resistant to the action of alkalies, and satisfactorily resistant to strong sulfuric acid. When water is present, corrosion is generally very rapid. The addition of silicon in considerable amounts produces an alloy, known by various trade names such as duriron, tantiron, ironac, etc., which is very highly resistant to corrosion. An efficient protective agent is the element chromium, either electroplated upon the metal, or still better used as an alloying metal in various proportions. The chrome steels have proven to be of very great value for chemical

industry, being highly resistant to chemical action and also possessing most of the other valuable qualities of steel. The properties of the silicon and chromium alloys will be given in some detail. The composition and properties of the common forms of iron are well known or may be readily found in texts on metallurgy.

**High-Silicon Iron.** — The addition of about 14.5 per cent of silicon to iron produces an alloy which is practically unaffected by sulphuric, nitric, acetic, phosphoric and cold hydrochloric acid as well as many other corrosive acid substances. The alloy can be fabricated only by casting and is so hard that it can be machined only with the hardest tools. It can be welded with the oxyacetylene flame, but only with difficulty. It is much more fragile than cast iron, which it resembles in appearance.

**Chrome-Iron Alloys.** — Alloys of iron with varying percentages of chromium are remarkably resistant to corrosion and have become known as "stainless steel" because polished surfaces of some of these alloys retain their bright appearance indefinitely even when exposed to the action of air, moisture or acids. Alloys of chromium and iron containing carbon in the percentages usually present in steel may be heat treated and therefore are known as *stainless steel*. When the carbon content is less than 0.10 per cent the properties of the chromium alloys are not altered by heat treatment, and they are therefore known as *stainless iron*. The addition of nickel to the iron-chromium alloy improves the working qualities of the alloy. These alloys may be classified as follows:

Type 1. Stainless steel — chromium content 11 to 13 per cent. Sufficient carbon for hardening purposes, usually from 0.30 to 0.40 per cent.

Type 2. Stainless iron — chromium content 11 to 14.5 per cent. Carbon content less than 0.12 per cent.

Type 3. Stainless iron with chromium content 16 to 20 per cent. Carbon content less than 0.10 per cent.

Type 4. Nickel-chromium-iron alloys. Composition may vary considerably.

Type 5. High chromium alloys having a chromium content of over 20 per cent.

*Resistance to Corrosion.* — In general, the resistance to corrosion of chromium alloys increases with the percentage of chromium. Chromium alloys are particularly resistant to the action of nitric acid and oxidizing agents in general, sulfides and organic acids. Caustic alkalies and alkali carbonates are without action. Chromium alloys are much less resistant to the action of hydrochloric acid and other halogen acids. Sulfuric acid in all concentrations up to 95 per cent attacks stainless alloys, but the action is inhibited by the presence of sufficient ferric or cupric sulfate. The so-called "mixed acid" which consists of strong sulfuric and nitric acids does not attack the high chromium alloys.

Stainless steels are resistant to corrosion only after heat treatment. Both chromium and iron form carbides which have a solution potential different from the solid solution of chromium and iron. Therefore alloys containing carbides are subject to corrosion. When the alloy is heated above the critical range the carbides go into solution and if the alloy is cooled sufficiently rapidly it will constitute a homogeneous solid solution which is resistant to corrosion.

The stainless irons which are low in carbon are superior to the stainless steels because carbides cannot form so that heat treatment is not necessary. While the stainless steels are hard and brittle, the stainless irons are tough and strong, so that many forms of apparatus may be fabricated for which stainless steels are not at all adapted.

*Use at High Temperatures.* — While with increasing chromium content resistance to corrosion increases, certain undesirable qualities from the manufacturing and mechanical standpoint develop so that the material becomes increasingly difficult to work. Alloys of this type are valuable for use at high temperatures. Alloys of type 3 will resist oxidation up to 870–950° C., depending upon the chromium content. Such alloys will also retain considerable strength at temperatures up to 700° C.

With chromium content over 20 per cent resistance to high temperatures increases. Alloys of chromium content of 25 to 30 per cent will withstand temperatures as high as 1150° C. for long periods.

*General Uses.* — The nickel-chromium-iron alloys may be readily welded and therefore may be used to fabricate apparatus for which the other alloys are not adapted. On account of the high cost of nickel, this alloy is quite expensive.

TABLE I. — PHYSICAL PROPERTIES OF TYPICAL STAINLESS IRON ALLOYS*

| Type | Composition | | | | Tensile Strength. Lbs./sq. in. | Yield Point. Lbs./sq. in. | Elongation (2 inches). Per Cent | Reduction of Area. Per Cent | Brinell Hardness | Treatment |
|---|---|---|---|---|---|---|---|---|---|---|
| | C Per Cent | Si Per Cent | Cr Per Cent | Ni Per Cent | | | | | | |
| 1 | 0.37 | 0.20 | 12.0 | 0.41 | 200,000 | 200,000 | 9 | 25 | 480 | Quenched at 900° C. and tempered at 500° C. |
| 2 | 0.10 | 0.19 | 11.5 | 0.35 | 180,000 | 160,000 | 18 | 50 | 350 | (a) Oil-quenched at 950° C. and tempered at 450° C. |
| | | | | | 73,000 | 40,000 | 37 | 75 | 150 | (b) Annealed at 800° C. |
| 3 | Under 0.10 | 0.60 to 0.90 | 16.5 to 18.5 | 0.21 | 75,000 to 80,000 | 55,000 to 60,000 | 30 to 35 | 65 to 75 | 150 to 170 | (a) Hot-rolled bars annealed |
| | | | | | 90,000 to 95,000 | 85,000 to 90,000 | 12 to 15 | 55 to 60 | 200 to 228 | (b) Cold-drawn bars |
| | | | | | 75,000 to 85,000 | 50,000 to 60,000 | 16 to 22 | | | (c) Annealed sheets and plates |
| 4(a) | 0.30 to 0.40 | 0.50 to 1.50 | 7 to 15 | 20 to 25 | 100,000 to 125,000 | 75,000 to 90,000 | 20 to 30 | 40 to 55 | 200 to 250 | (Krupp type) |

* Stainless Steel and its Application to Chemical Plant Construction. W. M. Mitchell, Ind. and Eng. Chem., v. 19, p. 1171.

TABLE I. — *Continued*

| Type | Composition | | | | Tensile Strength. Lbs./sq. in. | Yield Point. Lbs./sq. in. | Elongation (2 inches). Per Cent | Reduction of Area. Per Cent | Brinell Hardness | Treatment |
|---|---|---|---|---|---|---|---|---|---|---|
| | C Per Cent | Si Per Cent | Cr Per Cent | Ni Per Cent | | | | | | |
| 4 (b) | 0.10 | 1.25 | 15 to 16 | 10 to 11 | 120,000 | 40,000 | 57 | 50 | 150 to 170 | (English type) |
| (c) | 0.20 to 0.30 | 0.30 to 0.50 | 18 to 20 | 8 to 9 | 120,000 | 70,000 | 35 | 50 | 250 | (a) United States and England, hot-rolled |
| | | | | | 90,000 | 45,000 | 60 | 75 | 170 | (b) Annealed |
| 5 | 20 per cent chromium or over | | | | 80,000 to 90,000 | 60,000 to 65,000 | 10 to 25 | 15 to 30 | 170 to 600† | Rolled |
| | Tank plates‡ | | | | 60,000 | 40,000 | 25 | 50 | | |
| | Castings | | | | 40,000 to 50,000 | 30,000 to 40,000 | 1 | 2 | 200 | (a) Type 5, annealed |
| | | | | | 95,000 to 100,000 | 65,000 to 75,000 | 19 to 22 | 30 to 35 | 170 to 180 | (b) Type 3, annealed |

† Depends on carbon content and heat treatment.
‡ Minimum requirements.

The strength of all of the chromium alloys is equal to or greater than that of steel and may therefore be used to replace this metal whenever resistance to corrosion is of importance. With some modification, the methods of fabrication used with steel may be employed with the chromium alloys.

Chromium-iron alloys of 16–20 per cent chromium have recently been used for the construction of nitric acid absorption towers and other equipment for handling this acid both dilute and concentrated.

## LEAD

**Corrosion.** — This metal is very largely used in chemical industry on account of its resistance to dilute and concentrated sulfuric acid as well as hydrofluoric acid. Nitric acid as well as hydrochloric acid, particularly hot and concentrated, act rapidly on lead, but it may be used with cold concentrated nitric acid and cold dilute hydrochloric acid. Sulfuric acid also acts on clean lead surfaces but the lead sulfate produced, being insoluble in the acid, remains as a coating on the surface protecting it from further action, unless the acid is hot and concentrated. Sulfuric acid up to 60° Bé. (77 per cent) has very little action on lead even when heated nearly to the boiling point, while when cold even concentrated acid (96 per cent) has little or no action.

**Strength.** — The tensile strength of lead is very low (2000–3000 lbs. per sq. in.) and it is also deficient in rigidity so that it is generally necessary to use other material of greater strength to support it. Lead tanks as well as sulfuric acid chambers are constructed in this manner. Wood and steel are commonly used as the supporting material. It has also been found possible to bond lead to iron and steel so that piping and similar apparatus can be produced having the strength of the ferrous metal used together with the resistance to corrosion of the lead.

Lead is also alloyed with antimony to increase its rigidity, the amount of antimony added being from 6 to 10 per cent. The resulting alloy is somewhat less resistant to corrosion than pure lead, but it is rigid enough for the construction of impellers, piping which must be rigid, and similar uses.

**Use in Sulfuric Acid Manufacture.** — The most important single use for lead in the chemical industry is in the manufacture

of sulfuric acid.   The walls, roof, and bottom pans of sulfuric acid chambers are constructed of lead.   Sheet lead is used, the joints being made gas tight by melting together the edges by means of a hydrogen flame.   If solder were used, the acid would quickly eat it out.   Wooden or steel frames are used to support the lead chambers which are suspended within the frame-work.   The Glover and Gay-Lussac towers are generally constructed of lead, as well as the necessary piping and conduits for the acid gasses. Recently acid proof masonry has been successfully used for the construction of Glover and Gay-Lussac towers in place of lead. The metal is so soft and lacking in rigidity that the walls tend to sag and buckle and develop weak spots or openings which are repaired by burning patches of sheet lead on the outside of the chambers.

**Other Uses.** — Lead is also used for equipment designed for use with some weak acids such as phosphoric acid, sulfite liquors and concentrated acetic acid.   Dilute solutions of alkalies have only a slight action on lead, while it seems to be the only metal available for use with moist ammonia.   One of the advantages of lead is the ease of frabrication of a great variety of equipment by a competent lead burner.

### COPPER

**Properties.** — Copper has a number of properties which render it valuable for the construction of stills, condensers, kettles, etc.   It has a tensile strength of about 35,000 pounds per square inch.   It has considerable rigidity and is not corroded by weak acids, particularly in the absence of oxygen.   It is very largely used for the manufacture of stills and other equipment for handling acetic acid, both dilute and glacial.   The conductivity of copper for heat is high and its melting point is sufficiently high to enable it to be used for direct fired equipment.

**Uses.** — Copper has found extensive use for distillation apparatus for alcohol and many other volatile substances.   It has been largely used for evaporators in the sugar industry as well as for condensers.   These users are based upon its high heat conductivity, permanence, and the ease with which it can be fabricated into tubing, still bodies, kettles, and similar shapes.

## MONEL METAL

**Composition.** — Monel metal is an alloy of the following average composition:

Nickel.......................................67%
Copper......................................28%
Iron, manganese, silicon, etc................. 5%

It is a single solid solution which looks and acts like a pure metal. It has the silvery white color of nickel. It was originally produced from an ore which contained the metals in the same proportions as in monel metal, but is now made by melting together the constituents in carefully controlled proportions.

**Strength.** — Monel metal has a tensile strength and hardness approximately that of steel, but is far superior to steel in resistance to corrosion. As it can be cast, forged, rolled, hot or cold, welded, machined and polished it can be used to replace steel where resistance to corrosion is desired. It may be soldered and brazed in the same manner as iron and steel. It may be annealed by heating to 900° C.

**Corrosion.** — Monel Metal is highly resistant to acids such as benzoic, citric, hydrofluoric, lactic, dilute phosphoric, picric (eold), salycilic, tartaric, hydrocyanic and carbolic as well as all fruit and fatty acids and phenols. It also resists well the action of dry chlorine, sulfuric acid, and sulfur gases. It does not resist the action of nitric, chromic, perchloric, hot picric or phosphoric acids, or such oxidizing salts as ferric sulfate, copper sulfate, mercuric chloride or molten zinc salts. Neither does it resist molten metals or molten sulfur. Monel metal resists excellently the action of ammonia, solutions of ammonium hydroxide, fused and dissolved caustic alkalies and carbonates, sea water, solution of neutral salts such as alum, sulfates, chlorides, etc., gasoline and mineral oils generally, cresols, photographic chemicals, urine, dry mercury, drying solutions, alcoholic and other beverages. It is not resistant to the action of hydrochloric and nitric acids, molten lead, potassium cyanide, fused or in solution, and sulfurous acid.

The action of boiling acetic acid is given in the following table:

LOSS PER SQ. IN. OF MONEL METAL AT THE BOILING POINT

| | Weight per Hour | Inches Penetration per Day |
|---|---|---|
| 10% acetic acid | 0.07 mg. | .000011 |
| 26% acetic acid | 0.08 mg. | .000013 |
| 56% acetic acid | 0.11 mg. | .000018 |
| 90% acetic acid | 0.12 mg. | .000019 |

Monel metal rods exposed for ninety days to the action of continually renewed 6 to 7 per cent sulfuric acid at 74° C., loses weight at the average rate of 0.0045 gram per sq. in. per day. This is equal to the loss of a layer 0.00003 in. thick per day or 0.1 inch in about ten years.

PHYSICAL PROPERTIES OF MONEL METAL

*Average Range of Tensile Properties*

| Material | Yield Point, lb./sq. in. | Tensile Strength, lb./sq. in. | Elongation in 2 in., per cent | Reduction of Area, per cent |
|---|---|---|---|---|
| Hot-rolled rods... | 50 to 75,000 | 85 to 110,000 | 28 to 55 | 45 to 65 |
| Cold-drawn rods.. | 60 to 80,000 | 87 to 96,000 | 30 to 40 | 50 to 65 |
| Wire, annealed... | | 60 to 75,000 | | |
| hard drawn. | | 110 to 150,000 | | |
| Castings......... | 32,5 to 44,000 | 65 to 85,000 | 25 to 45 | |
| Annealed sheet... | | 60 to 75,000 | 30 to 40 | |

Brindell hardness (3000 kg. load).....................140–160
Specific gravity, cast.............................8.87
           rolled.............................8.98
Electrical conductivity relative to copper............4 per cent
Heat conductivity relative to copper.................6 per cent
Coefficient of thermal expansion 20 to 400° C.........0.000015
Specific heat, 20° to melting point .................0.127 calorie per gram
Latent heat of fusion.............................67 calories per gram
Modulus of elasticity.........................22–23,000,000 lbs. per sq. in.
Maximum shearing stress, hot rolled.................60–70,000 lbs. per sq. in.
Maximum shearing stress, cast metal...............40–50,000 lbs. per sq. in.

**Uses.** — The features of the metal which recommend it for industrial purposes, especially in the chemical field, are its resistance to corrosion, the bright nickel finish which it takes and retains, its strength and hardness, particularly at high temperatures, and its resistance to erosion by water and steam.

It is used in the manufacture of sheet, bars, wire, wire cloth, screens, nails, chain, bolts, nuts, castings, roofing material, also for pumps, pump liners, rods, valves for handling sea water, mine water, and acid and alkaline corrosive solutions generally. It is also employed to make pickling tanks and crates for the pickling of steel, construction of mining machinery, mine screens, dyeing machinery and equipment, and in the chemical and oil industries for miscellaneous parts which are exposed to severe corrosive conditions. It also makes splendid filter cloths for industrial purposes.

### ALUMINUM

**General Properties.** — Aluminum is a white metal resembling tin in color but very much lighter in weight. It has a fairly high resistance to chemical action. Its resistance to the action of acids, particularly weak organic acids, makes it greatly superior to iron, copper, and brass. It has the additional advantage that its salts are non-toxic and being colorless do not discolor other products. Aluminum tarnishes in damp air, an almost invisible coating of oxide being formed which is very permanent and prevents further attack. This protective coating undoubtedly accounts for the high resistance of aluminum to chemical action.

**Corrosion.** — Aluminum is not attacked by the common organic acids, acetic, citric, tartaric, etc., and many organic compounds. Formic acid is an exception to this rule. Even $\frac{1}{2}$ to 1 per cent of formic acid in acetic acid will cause rapid destruction of aluminum apparatus. Acetic acid of from one to ten per cent concentration corrodes aluminum. Slightly stronger acid has only slight action. This is also true of acid of less than one per cent strength. A great deal of aluminum equipment is used for the manufacture of these acids and their products. Aluminum has the property of resisting the attack of sulfur compounds and therefore finds extensive use in the rubber and petroleum industries.

Concentrated $HNO_3$ has very little action upon the metal unless it is impure; but more dilute acid dissolves it appreciably. Sulfuric acid reacts with the metal only when hot and concentrated. HCl, dilute or concentrated, and hydrofluoric acid under the same conditions dissolve it readily with evolution of hydrogen. Dilute $H_2SO_4$ attacks the metal very slowly. Alka-

lies and the hydroxides of the alkaline earths, especially barium hydroxide, attack the metal. Dry ammonia gas has no action; solution of ammonia has a slight action upon the metal, converting it into hydrate. The fixed alkali carbonates attack the metal. Solutions of chlorine, bromine and iodine rapidly corrode the metal. It is very slightly acted on by salt water, and not at all by $CO$ or $CO_2$.

The common metals are all electronegative to aluminum in a voltaic couple and care should be exercised that aluminum when exposed to water or aqueous solutions shall not come in contact with any other metal that will cause corrosion by galvanic action.

Tubing can be thoroughly insulated by employing rubber gaskets, washers and bushings, and sheets and shapes can be insulated from other metals by using heavy paint or asphalt between the joints.

Alkaline solutions in most cases are quite corrosive to aluminum and its alloys. Ammonia and soap solutions are an exception to this rule.

### PHYSICAL PROPERTIES

| | |
|---|---|
| Specific gravity, cast | 2.66 |
| melted | 2.54 |
| Thermal conductivity at 0° C. (Ag=100) | 31.33 |
| at 100° C. | 32.40 |
| Coefficient of expansion at 40° | 0.00002313 |
| at 600° | 0.0000315 |
| Melting point | 657° C. |
| Specific heat, 0° to 100° C. | 0.2270 |
| Electrical conductivity 98.5% pure (Cu=100) | 55 |
| 100% | 66 |
| Tensile strength, cast metal | 15,000 lbs. per sq. in. |
| drawn metal | 35,000 lbs. per sq. in. |

The tensile and compressive strengths of aluminum (99 per cent pure) average as follows:

### TENSION

| | Elastic Limits lbs. per sq. in. | Ultimate Strength lbs. per sq. in. | Reduction of Area (Per Cent) |
|---|---|---|---|
| Castings | 8,500 | 12,000–14,000 | 15 |
| Sheet... | 12,500–25,000 | 24,000–40,000 | 20–30 |
| Wire... | 16,000–33,000 | 25,000–55,000 | 40–60 |
| Bars... | 14,000–23,000 | 28,000–40,000 | 30–40 |

**Uses.** — While the tensile strength of aluminum per square inch is quite low, its strength on the basis of weight approaches iron and steel. The price per pound is considerably higher than that of such common metals as iron, lead and copper but on account of its low specific gravity the cost of unit volume is not much greater than that of the other metals mentioned. The equipment constructed of aluminum includes tanks, stills, heating coils, piping, etc. It is used extensively in acetic acid plants.

### CHEMICAL STONEWARE

**Composition.** — Chemical stoneware is a ceramic material made of carefully selected clay, moulded and fired. It is essentially an aluminum silicate partly combined and partly mixed with other silicates. The composition of the average material is as follows:

|  | *Per Cent* |
|---|---|
| Silica ($SiO_2$) | 73.23 |
| Alumina ($Al_2O_3$) | 22.27 |
| Iron ($Fe_2O_3$) | 0.58 |
| Lime ($CaO$) | 0.58 |
| Magnesia ($MgO$) | Trace |
| Potash ($K_2O$) | 2.02 |
| Soda ($Na_2O$) | 1.42 |
| Loss on ignition | 0.06 |

Physically, stoneware is an aggregation of more or less refractory particles of ceramic material in various stages of fusion called "grog," bonded together by means of a vitrifying clay, usually with the addition of a flux. The physical properties of the material can be modified between very wide limits by varying the size of the particles and the nature and proportions of the grog, clay and the flux. The coarseness and porosity may be varied from such a porous product as a fire brick to as fine and dense a product as porcelain. The more porous bodies are more resistant to sudden changes of temperature. Consequently, when the ware has to withstand extremes in temperature, as in pipe lines for carrying off the hydrochloric acid gas from salt cake-furnaces, or in the supports for the basins in a sulfuric acid cascade concentrator, a porous ware is selected. Where a non-porous material is required, as in the electrolytic refining of precious metals, a porcelain-like ware is furnished.

Between these two extremes it is possible to develop a ceramic material to fulfil the requirements of most chemical operations.

**Resistance to Corrosion.** — Chemical stoneware is the most durable of all clay products. It is extremely hard and dense, and steel will strike a spark from it just as it does from flint. It is an electric insulator and insulators made of a special grade of stoneware have been used for experimental purposes at a potential as high as 600,000 volts. It resists the action of all acids and other corrosive materials encountered in industrial work. The only exceptions are those materials which also attack glass — that is, hydrofluoric acid and hot, strong caustic alkalies, which also have a slight surface action on this ware just as they have on glass.

The use of chemical stoneware removes the corrosion problem entirely for a great many very corrosive liquids. Chemical stoneware is usually glazed to give it a smooth attractive appearance. The acid resisting properties of the stoneware are not due to the glaze, but are dependent upon the composition of the stoneware itself.

PHYSICAL PROPERTIES

Tensile strength......................1000 to 2500 lbs. per sq. in.
Compressive strength...................25,000 to 80,000 lbs. per sq. in.
Modulus of elasticity...................6,000,000 to 10,000,000 lbs. per sq. in.
Thermal conductivity (B.t.u. per hr. per
   sq. ft. per °F.).......................0.6 to 0.9
Specific heat..........................0.185 to 0.190
Specific gravity.......................2.06 to 2.36
Coefficient of expansion (°F.)............0.0000023 to 0.0000027
                         (°C.)............0.0000031 to 0.0000048

The tensile strength is low as compared with most metals while the compressive strength is high. This must be taken into account in designing equipment of this material. The thermal expansion and conductivity is much lower than that of the metals, being about that of glass.

**Uses.** — As chemical stoneware apparatus is molded out of soft clay and worked up by hand into the shape desired, it is possible to produce apparatus of any desired shape and size within the limits of the strength of the material. After the stoneware has been fired, the surfaces may be ground and polished so that valves and similar apparatus which require gas-tight joints may be constructed.

Unless stoneware is accidently broken, it is very durable because it is so highly resistant to corrosion. For this reason depreciation and cost of repairs is very low for this material. On account of its high resistance to chemical action, contamination of the product is reduced to a minimum. The use of stoneware is limited by the size of individual pieces which can be fabricated and transported, the breakage in transportation and erection, and its inability to stand rapid temperature changes.

A very considerable variety of stoneware apparatus is in use, including tanks, piping, valves, condensers, scrubbing towers, filters, kettles, etc. High speed machinery such as exhaust fans and blowers for handling corrosive gases such as hydrochloric acid, chlorine, nitric acid, sulfur dioxide, etc., are constructed in such a manner that all parts coming in contact with the gases are made of stoneware.

High-speed centrifugal pumps are constructed of chemical stoneware for handling corrosive liquids such as sulfuric, muriatic, nitric and other acids and corrosive salt solutions.

## GLASS

**General Properties.** — Glass has always been used in chemical industry to a limited extent. One of its great advantages is transparency, by which operations can be seen and therefore more readily controlled. On account of the fragile nature of glass its use in manufacture has been very often confined to short pieces of tubing or sight glasses conveniently placed for observation.

The insolubility of glass, particularly in acids, has led to its use for condenser tubes and similar apparatus where highly acid vapors must be dealt with.

*Boro-Silicate Glasses.* — Recently glasses have been developed possessing a combination of qualities which renders them superior in many respects to any glass heretofore available. This has led to a much greater use of glass in chemical industry. These glasses, sold under the trade-name of *Pyrex*, are boro-silicate glasses having very low thermal expansion and very high resistance to chemical action. They contain no metals of the magnesia-lime-zinc group and no heavy metals. Contamination of the product from any of these metals therefore need not be feared. The low coefficient of expansion renders this glass resistant to suddent changes in temperature, such as immersion

of glass at 300° C. into water at 5° C.   This glass may be used continuously at temperatures as high as 600° C. and for short periods at somewhat higher temperatures.

**Corrosion.** — The resistance to chemical action is shown by the following tests: Concentrated sulfuric acid at its boiling point dissolves in four hours 0.000002 gram of glass per sq. cm. per hour.   Constant boiling hydrochloric acid dissolves 0.000006 gram of glass per sq. cm. per hour.   No measurable action is shown by acetic anhydride after five hours at the fuming temperature.

Hydrofluoric and glacial phosphoric acids are the only acids which have any appreciable action on pyrex.

Alkalies show a somewhat greater action, which increases with the temperature and concentration.   After six hours boiling, 5 per cent caustic soda produces a loss of 0.0022 gram of glass per sq. cm., while 35 per cent caustic soda gives a loss of 0.0032 gram per sq. cm.   Twenty per cent caustic soda at 49° C. for 100 hours produces a loss of 0.00246 gram per sq. cm.

**Thermal Conductivity.** — While the thermal conductivity is only 0.0027 c.g.s. unit, experiments show that *Pyrex* condenser tubing will transmit 2/5ths as much heat as copper heating.   In plant operations, values for transfer of heat from liquid to liquid as high as 125 B.t.u. per square foot per hour per degree F. have been obtained.   *Pyrex* condenser tubing has come into very extensive use and is proving very satisfactory for some purposes. The dielectric strength and electrical restivity of pyrex is very high.

PHYSICAL PROPERTIES OF PYREX GLASS

Linear coefficient of expansion, 19–350° C.........0.0000032
Elasticity coefficient............................6230 kg. per sq. mm.
Hardness.........................................scleroscope, 120
Specific gravity.................................2.25
Specific heat....................................0.20
Refractive index.................................1.4754

## FUSED SILICA

**General Properties.** — Fused silica is a vitreous material produced by heating to a high temperature quartz or other forms of pure silica, $SiO_2$.   This material softens at 1400° C. and melts at 1750° C.   On account of the extremely high temperature

required for its production it is difficult to produce large pieces of fused silica apparatus.

This material has several very remarkable properties. It is almost completely insoluble in most of the common acids in any concentration either hot or cold. It has a very high melting point and has an extraordinarily small coefficient of expansion so that it can be heated to a very high temperature and is not injured by rapid cooling. Red hot apparatus may be cooled by a stream of cold water without injury. While possessing considerable mechanical strength it is very brittle, so that fused silica must be very carefully protected from mechanical injury.

**Resistance to Corrosion.** — As far as can be determined, fused silica is completely insoluble in distilled water, no other known material possessing its resistance to the solvent action of pure water.

Sulfuric; nitric; hydrochloric; hydriodic; hydrobromic; arsenic and chromic acids have no action on this material regardless of concentration or temperature. The halogens are also without action. Phosphoric acid has a slight action, while hydrofluoric acid attacks it to about one-tenth the extent of its action on glass. Melted zinc, cadmium and tin in contact with fused silica do not attack it appreciably. It is attacked at room temperature by alkaline solutions to a smaller extent than the best grade of glass, but at higher temperatures it is readily attacked by alkalies.

All fused quartz when exposed to high temperatures tends to revert from the vitreous to the crystalline state. Work in this connection led the National Physical Laboratory of London to conclude: "In general, the loss of strength hardly commenced at 1120° C.; at 1188° C. it existed, but was not very serious, even after eight hours heating; but four hours heating at 1350° C. produced a reduction of 40 per cent to 50 per cent in strength, showing that the rate of loss of strength increases very rapidly as the temperature rises." Therefore, for continuous operations fused silica cannot be exposed to temperatures over 1200° C., but for short periods of time the material may be successfully employed at much higher temperatures.

PHYSICAL PROPERTIES

Specific gravity..............................................2.07–2.22
Coefficient of expansion per degree C......................0.00000054
Melting point...............................................1750° C.
Softening point.............................................1400° C.

**Uses.** — Fused silica dishes are extensively used for the concentration of sulfuric acid. It has also been extensively used for the construction of absorption apparatus for muriatic acid. It is also used for a variety of other apparatus.

### CEMENT AND CONCRETE

**Portland Cement.** — Portland cement is a solid solution of di- and tri-calcium aluminates and silicates produced by heating to incipient fusion a finely ground mixture of materials rich in lime on the one hand and alumina and silica on the other, such as limestone and clay. The clinker formed is ground to a fineness such that 92 per cent will pass a 100 mesh sieve. In order to retard the setting of the cement from 2 to 3 per cent of anhydrous calcium sulfate is added during the grinding.

**Composition.** — Cement of good quality usually falls within the following limits as given by Meade:

|  | Limits % | Average % |
|---|---|---|
| Lime | 60–64.5 | 62 |
| Silica | 20–24.0 | 22 |
| Alumina | 5–9.0 | 7.5 |
| Magnesia | 1–4.0 | 2.5 |
| Iron oxide | 2–4.0 | 2.5 |
| Sulfur trioxide | 1–1.75 | 1.5 |

A definite ratio must be maintained in the manufacturing process among the lime, silica, iron and aluminum oxides in order to produce the calcium aluminates and silicates upon which the setting properties and strength of the cement depends.

In these ratios the iron and aluminum oxides are interchangeable, as these oxides function as acid radicals. The basic radical, calcium oxide, may also be replaced, to a certain extent, by magnesium oxide although the presence of this base somewhat modifies the properties of the cement. The magnesia should not exceed 4 per cent.

The ratio between the molal percentages of lime and the combined percentages of silica, alumina and iron oxides should not fall below 1.9 or above 2.1.

$$\frac{CaO}{SiO_2 + Fe_2O_3 + Al_2O_3} = 1.9 \text{ to } 2.1.$$

The ratio of silica and alumina should be as follows:

$$\frac{SiO_2}{Al_2O_3} = 2.5 \text{ to } 4.$$

**Setting.** — When mixed with water, cement sets and gradually hardens into a stone-like mass. If mixed with sand, gravel or stone, and water, it acts as a cementing agent to bind these materials into a stone-like mass, known as concrete. If the concrete is poured around bars, it will, when set, adhere to these bars, and is then known as reinforced concrete.

The setting of cement is due to the hydration of the calcium aluminates and silicates present in the cement. The reactions are as follows, the aluminate being acted upon first:

$$(CaO)_3Al_2O_3 + 12H_2O = (CaO)_3Al_2O_3.12H_2O,$$

$$(CaO)_3SiO_2 + 4\tfrac{1}{2}H_2O = CaO.SiO_2.2\tfrac{1}{2}H_2O + 2Ca(OH)_2.$$
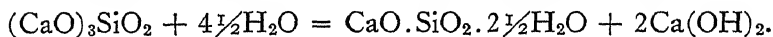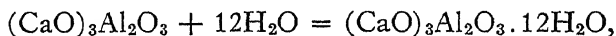
The hydrated compounds are in a gelatinous colloidal condition which forms an adhesive coating around the grains of cement and serves to bind the sand grains together. This produces the initial set of the concrete. The free water gradually diffuses through the colloidal coating of the grains of cement and in time completely hydrates the cement.

The cement gel gradually hardens as it dries out, and binds the grains of sand together more firmly. As this cement gel is an irreversible colloid it cannot be again softened by water. The strength of the concrete is therefore not reduced by immersion in water.

As the cement grains are acted upon by water they tend to swell on account of the production of the cement gel. In this manner the voids between the sand grains are filled up. If too much water is added to the mixture the concrete produced is weakened, probably due to the formation of a porous mass which the cement gel cannot fill when finally dry.

The free lime produced undoubtedly aids in the initial set of the cement and also in the final hardening by conversion into carbonate. The presence of gypsum tends to retard the setting of cement. This is probably due to the fact that calcium sulfate is an electrolyte and as such tends to prevent the hydrated aluminate from precipitating from its sol to form a gel. This

retardation of the coagulation probably assists in the more nearly complete hydration of the tricalcium aluminate by facilitating the diffusion of the water through the outer coating of the cement grains.

**Concrete.** — *Uses.* — Concrete is used very extensively in all plants for foundations and construction of buildings as well as for settings for heavy apparatus of all kinds.  It is eminently satisfactory for these purposes.  For strictly chemical engineering uses it is very largely used for the construction of tanks for a variety of purposes.

Concrete is not acted upon by ammonia or alkaline solutions or dilute acids.  Vegetable or animal oils have a tendency to disintegrate the concrete by the formation of lime soaps.  Unless care is taken in mixing and tamping down the concrete, it will not be water-proof.  The most satisfactory results are obtained by continuous construction so as to avoid the formation of joints. Frerichs [1] has described the construction of large tanks for ammonia by continually and gradually raising the forms and adding the concrete mixture continually until the tank is completed.

*Proportioning.* — Strength and imperviousness are the two qualities of concrete with which the chemical engineer is most concerned.  With given aggregates and quantity of cement, the mix producing the greatest density will have the greatest strength.

The final strength of concrete bears a definite relationship to the ratio of its water-cement content at the time of mixing and placing as long as a workable mixture is obtained.  This strength can be predetermined with remarkable accuracy providing some measure of control of mixing, placing and curing is exercised. For example, six gallons of water per sack of cement in a plastic mix will yield a concrete which will have a strength of about 2400 lbs. per sq. in. in 28 days.  Similarly, 5.25 gallons of water per sack of cement will yield a unit strength of 3000 lbs. in a similar period.  Proper allowances, must, of course, be made for the moisture in the aggregates.

The cement and the water are the only ingredients of concrete which enter into chemical combination and affect the strength. The sand and gravel or stone are inert and serve only to increase the bulk and therefore affect the economy.  This being the case,

[1] Trans. Am. Inst. Chem. Eng., vol. XI, p. 203.

it is possible to "design" an economical mix very simply in the following manner: Mix a small quantity of cement (25 or 50 lbs.) on a water-tight tray or platform with the proper proportion of water to give the strength desired. Add sand and gravel or stone in measured quantities to this paste until, with continuous mixing, the mixture reaches the consistency desired. The quantities of cement, sand, stone, and water are now all known and their ratios represent the best proportions for those particular aggregates.

Graded sand and graded stone will give the smoothest and most economical concrete. An excess of stone gives a harsh and unworkable mixture. An excess of sand requires a proportionately greater amount of water for lubrication and lowers the economy.

*Mixing.* — Concrete should be mixed for one full minute in a batch mixer or turned over at least six times after water is added, if mixed by hand.

*Placing.* — Concrete should be placed as close to its permanent location as possible and not allowed to flow in the form. Flowing may separate the aggregates. The concrete should be spaded at the form to release entrapped air.

*Curing.* — Newly placed concrete should be protected from freezing for at least 72 hours after placing.

Concrete should be kept moist by sprinkling or ponding for fourteen days after pouring to obtain the greatest strength.

*High-Early-Strength Concrete.* — The delay of waiting for ordinary concrete to attain sufficient strength to carry its intended load has led to the development of patented cements containing alumina which will make a strong concrete in 24 hours. Increasing the proportion of ordinary Portland cement by three or four will also give a very strong concrete in two or three days. The expense of these expedients limit their use to work of small proportions. Concrete can now be purchased, mixed and delivered to the job in agitated tank trucks.

*Water Proofing.* — Various methods have been adopted for making the concrete impervious to liquids. These methods may be divided into classes as follows:

Integral water proofing in which the water proofing material is added to the concrete during the mixing. Metallic soaps and mineral oils have been used for this purpose.

Various coatings have been applied to the surface of the hardened concrete.    These include hydrocarbons such as paraffine, tar and asphalt.    These substances are either applied hot or as a paint.    Coatings of this kind are particularly resistant to acid liquors.    Sodium silicate solutions are applied in a similar manner.    Deposits of silica are formed in the interstices of the concrete, rendering it impervious to most liquids.    Silicate treatment of concrete floors renders them non-dusting.

Concrete tanks are often used for the crystallization of salts and for this purpose are more valuable than wood because the heat is lost more rapidly.    Such tanks are constructed with hopper shaped bottoms with suitable drain pipe and drop door for removing the crystals.    The crystals are frequently dropped into centrifugals for the removal of the mother liquor.

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# CHAPTER XV

## COSTS AND FINANCING

G. A. PROCHAZKA, Jr., E.M.

**Fundamental Concepts.** — A chemical process to have commercial value must yield goods which can be sold at a profit. If the efforts in chemical engineering are to be properly directed, it is necessary for the engineer to become familiar with the more salient features of commercial life. Cost, today, is the leader of the triumvirate that rules business; selling price and profit, however, are scarcely less important. To round out the engineer's knowledge of mercantile enterprise he must also become acquainted with some of the rudimentary facts pertaining to the financial management of a business. These four things, selling prices, profits, costs, and financing will now be discussed in turn.

People often imagine that a manufacturer produces goods, figures out the cost of making them, adds a comfortable margin of profit and accepts the final figure as his selling price. Unfortunately the thing is not quite so simple. The problem of selling prices must often be approached from a different angle. Consider that an almost unlimited number of articles are made specifically for the 5 and 10 cent store trade. Years ago Henry Ford decided to make an automobile to suit the purse of the poor man. Further familiar examples of manufacturing to a price could be given. We find that today a large part of the wares of commerce are made either to sell at a given price or they are made because an existing selling price appears to allow a comfortable margin of profit.

Two other restrictions may prevent the setting of selling prices at desired levels. With nearly every article, at some point in the rising scale of prices, we find consumption reduced through the use of substitutes. When prices get too high, the marketability of a product may come to an end. The other limitation to selling prices is to be found in that people have developed a sense of values and it is not easy to alter these fixed views. An article may bear only a slight resemblance to another product which has

469

been on the market for a long time at a much lower price, yet that slight connection may be enough to make the former unsaleable at a proper price. It would cost more than could ever be gotten in return to prove to the masses that the former article cannot be made so as to sell at a lower price.

Finding selling prices confined to levels beyond which they cannot be raised, producers turn to other means for increasing their profits. One of the most prevalent yet ill advised expedients is to cut prices with the expectation that a greater sales volume will bring in a greater total profit in spite of the fact that the margin per unit has been reduced. The usual end to this procedure is anything but satisfactory. Competitors follow suit and the reductions continue until the majority of the makers commence to show red ink figures on the balance sheet. Everybody finally has the same old customers but at much lower prices. To get back to profitable figures requires an economic upheaval. The safer path of improving the quality and expanding the consumption should not be overlooked.

Reducing costs is a popular method of increasing profits. Efforts of this kind can be applied in two directions. In the chemical industries research is constantly directed towards improving the output from a given amount of raw material and towards the use of cheaper materials. The other approach to this problem is through a revision of the cost structure of a business. In other words, the theoretical background of a particular process is not changed but an effort is made to find more economical means of handling the existing proposition in the plant. Unnecessary activities are eliminated, material handling is arranged in a less costly manner, the size of the operations in existing machinery is increased, other products are sought out for manufacture in the same apparatus, and many other things are carefully examined, for often the saving is obtained through changes which are so close to us and are so simple that in spite of their obvious nature they are passed by unnoticed.

One phase of commercial life spreads considerable mental confusion among the uninitiated, merely because the apparent business is not the true money making factor in the enterprise. For instance a chain store may appear to be doing well, when, if the truth were known, it would be found that the organization could not exist without the profits coming from the real estate leasing end of the business. The sale of merchandise adds to the

profits but does not stand alone as a separate venture. This situation is strongly accentuated in the chemical industries with their numerous by-products. There are two extreme views to the marketing of by-products and in practice we find many situations which are intermediate to them. In one case the revenue from the by-product is looked upon as so much salvage. The sum so realized may or may not be deducted from the cost of producing the major article. The other position demands that every by-product bring in its share of profit. A by-product may be superior or inferior to the same article placed on the market by direct manufacture, and further it may become the major product. In these situations it is necessary to diagnose carefully just what the competition is doing.

A few thoughts as to the nature and characteristics of profits are not amiss here. According to the economists there are four kinds of profits: ordinary, monopoly, speculative and aleatory or chance. The source of profits should be clearly recognized. A manufacturing enterprise draws its subsistence from ordinary profits even though many a time a bad situation has been cleared up by a substantial influx of one of the other types. It also should be borne in mind that big risks require big profits and that quick turnovers are usually made by accepting short profits.

The profit margin that lies between a given selling price and cost is often measured and contrasted with other profits in an incorrect way. Just as sales commissions are figured as a per cent of selling prices, profits are often studied in the same terms. This practice is dangerous and misleading. In order to understand why this should not be done it is necessary thoroughly to grasp the basic principles of manufacturing.

The fundamental thing which the manufacturer has to offer his customers is a superior knowledge of how to perform certain processes coupled with the facilities for their proper execution. Barring unusual circumstances, the customers can go out and buy the same raw materials at approximately the same prices. Whenever the manufacturer charges too much for his product he invites competitors to take up that manufacture. If he is accustomed to studying profits in terms of selling prices he is apt to charge too much or too little for any new article in which the ratio of material to process cost is substantially different from the ratios that represent his normal operating experience.

This thought of knowing when a profit is properly proportioned can be explained more easily by considering some actual figures. Take two articles in which the following figures obtain:

| Article | No. 1 | No. 2 |
|---|---|---|
| Material cost | $0.25 | $0.75 |
| Process cost | .75 | .25 |
| Factory cost | $1.00 | $1.00 |
| Gross profit | 1.50 | 1.50 |
| Selling price | $2.50 | $2.50 |
| Profit as a per cent of selling price | 60% | 60% |
| Profit as a per cent of process cost | 200% | 600% |
| Ratio of selling price to material cost | 10 | $3\frac{1}{3}$ |

For the same amount of factory work we try to fasten three times as much profit on Article No. 2 as on Article No. 1. These figures show far more clearly than words the extreme importance of having profits adjusted to the element which is really being sold when one is engaged in the manufacturing industries. It is desirable and necessary to take some profit on raw materials to reimburse the manufacturer for the risk in handling them; but he must make sure that he is not taking an amount that seems unreasonable to his customer or a sum that leaves the door wide open to his competitor to cut under him and get the business away from him. If the manufacturer is not accustomed to measuring his profits in terms of pure process costs he will find himself some day doing all the unprofitable work while other people are selling the articles that pay dividends to the stockholders.

Cost Accounting. — To recognize clearly that the manufacturing end of a business deals with two major components, materials and process changes, makes the art of cost accounting easier to understand. To make such divisions as material, labor and expense really confuses the major issue because labor and expense are two partially interchangeable quantities. For instance, if excavating is done by pick, shovel and wheelbarrow, the cost of this work is predominatingly a labor item; but if the work is done with a steam shovel the cost of the work is essentially created through charges of the expense type, such as taxes, insurance, depreciation, supplies, etc. Excavating is a process and the way the process is performed depends entirely on the

magnitude of the undertaking. To investigate the underlying details as to how the work was performed is an entirely necessary act, but to investigate them before the major outlines of the proposition have been defined only leads to useless confusion.

The preceding paragraph illustrates the most vital point in cost accounting, namely the importance of exact thought. Orderly effort almost transcends exact thought. The reason why these two arduous requirements exist will become clear when we consider the theoretical background of the science.

The simplest problem in cost accounting is met when we deal with a business making only one product, for then we are not called upon to unravel numerous intertwined values in order to arrive at article costs, the ultimate goal of our efforts. This elementary situation, unfortunately, is an oddity in practice. We must probe deeper to supply the needed knowledge as to costs. The path open to us is to study functions and to evaluate the cost of performing them. That there are difficulties in this will become apparent as we go on.

Let us take the case of a small machine shop mainly using bench lathes in a rented loft. Here the easiest method for calculating costs would be to check the material and labor against each job. The expenses (rent, light, power, etc.) would be small, they would vary directly with the hours of labor and they could be charged to each job on that basis, producing a result closely approximating the true factory costs.

As an example in the chemical industry we will take up a small plant with two departments. One of these uses little labor and a large amount of process steam, whereas in the other department the reverse condition exists. Using the method which was so satisfactory for the machine shop we arrive at an entirely erroneous result. The department with the large labor force pays for most of the process steam, yet the process steam was consumed by the division with the small payroll. It is easy to imagine a small factory working under the conditions of the machine shop growing into the situation depicted by the chemical plant. Cost methods must be varied to meet changes taking place within an enterprise.

If we want to avoid the pitfalls of incorrect cost accounting, we must clearly understand that practical considerations constantly require us to find serviceable answers which approximate the truth within close and reasonable limits. The limit of error

is different in every industry, is different in every plant and is different within the same plant whenever the manufacturing methods are changed.   This situation has a direct bearing on the organization of departments and on the distribution of costs.

**Plant Departmentalization.** — After a plant has grown to the point where its expenses are no longer directly proportional to the hours of actual process labor, we must subdivide the expenses, and distribute each class according to some factor which varies in a known, yet simple manner, with the output of the factory. Departmental organization offers the most rational solution to this problem.   Departments are a natural offshoot of factory administration and only in recent years have been recognized as a convenient tool for cost accounting.   From the viewpoint of their relation to manufactured articles, departments may be divided into three classes: commercial, service, and production. These differ in that the costs of the commercial departments cannot be charged to specific articles, that the costs of the service departments are in some part indirectly chargeable to specific products, and that the costs of the production departments are directly chargeable to specific articles.

The proper subdivision of the commercial, the service and the production departments depends entirely on the conditions found in a particular business.   The adopted classifications must be correct, useful and practical as to the limits of refinement in division.   Such well known activities as administration, sales, office, and warehousing lead to the development of the corresponding departments.   Service departments are dictated by the volume of activity residing in such functions as transportation, mechanical construction, power, applied technology, supervision, etc.   The production departments are determined by the nature of the processes conducted in the factory and not by the products made, even though at times the two thoughts seem to be identical. More attention will be given to the various branches of the business organization when their relation to costs is discussed.

The picture which we now have before us is that of a business correctly divided into a number of departments.   It is immaterial whether these divisions actually exist as such or are just imagery created for cost purposes.   For the moment we will accept without further thought the fact that we must purchase raw materials if we are to operate the factory and concentrate

our attention on all the other things which we must buy if we are to keep the plant running. These expenditures, actual in nature, or just paper calculations estimating the dissipation of capital assets, vast in number though they be, can be grouped into a small number of clases as follows: depreciation, taxes, insurance, expenses, supplies, and labor.

**Depreciation Charges.** — Depreciation charges are added to factory costs to cover the values lost through wear and tear. A fusion kettle is good for 500 melts; a set of dies will stamp out 100,000 articles; a power press will last 20 years: these are the thoughts that come to us when we think about depreciation. Every machine will do a certain amount of work and then it is too worn out to supply any further useful service. The dissipation of such fixed assets as buildings, machinery, tools, etc., plays a vital part in article costs and appropriate charges must be included to cover these losses.

Depreciation can be calculated on either a time or output basis. The latter method is simple. A proportionate part of the original cost is charged to each unit produced. The first method is not so simple and is open to much controversy. When depreciation is taken on a time basis, the life of the unit is estimated and a corresponding amount of the first cost is charged to production each year. There are two popular methods for doing this. One is called straight line depreciation because the charges for each year of useful life are equal. The other takes diminishing balances into consideration and each year writes off a fixed percentage of the residual undepreciated value. Costs obtained in this way will decrease in amount each year.

The principal difficulty with depreciation taken on a time basis is to find the true life term of the machine. Interesting tables setting forth the probable life of many kinds of assets are available. The "Accountants Handbook" of the Ronald Press company has a section devoted to rates and other elements of depreciation. In using such values we must realize that it takes a large set of figures to produce a safe average, that we will be using relatively few machines of a given type, and that anyone of them might be an unusual extreme case.

*Obsolescence.* — In addition to depreciation we must give some attention to obsolescence, a subject closely associated with it. Simplified production methods and changing fashion will often

end the useful life of a machine before it is worn out. The unfortunate feature of obsolescence is that we cannot calculate the exact time when its influence will terminate profitable production. When obsolescence appears to be one of the industrial risks, to be on the safe side, high depreciation rates should be used.

*Repairs and Renewals.* — Repairs and renewals are two elements closely related to depreciation. Whenever we repair, or renew the parts of a machine we extend its life. Repairs can be dismissed as the more or less trivial maintenance items or as the constant upkeep costs which are a proper charge against production, the added term of service having been discounted in the depreciation rates. When new parts are put into a machine, this transaction should be held as a renewal because we have extended the life of the machine beyond the point provided for by the depreciation rates. In practice it is hard to say at all times just when a charge is a repair or when it is a renewal. Common sense must set these boundaries.

*Depreciation Accounts.* — There are a number of points of interest in regard to the bookkeeping procedure for these cost elements. Depreciation charges are not deducted from first cost accounts because that act would distort unnecessarily the Buildings, Plant, Tool, etc., accounts. The common practice is to open an account called Reserve for Depreciation to which these costs are credited when the corresponding amount is charged to production. Money coming into the business in this way ordinarily is not kept apart, but is used in purchasing stock and in the payment of current bills. The account Reserve for Depreciation, therefore, is not really a reserve, but figures in financial statements as an offset used to reduce the first cost values of the fixed assets to their true present value. Repairs, as was previously noted, are charged to current production. Renewals on the other hand are not charged to current production, but are set up as an asset which in financial statements is used as an increment to the first cost accounts to show that their life has been extended. This asset value is extinguished by carrying on depreciation charges until the renewals have been wiped out. By doing the bookkeeping in this way we obtain more uniform costs, and make costs easier to understand.

**Taxes and Insurance.** — Taxes and insurance can be grouped together in figuring costs because a single annual calculation will

settle the amount chargeable to each department. Taxes, here refers to local assessments and not to Federal or state income taxes which are deductible from profits and do not constitute a cost element. Real estate taxes can be allocated in proportion to building values and personal taxes can be disposed of conveniently by charging them according to plant values. Insurance, here, refers only to fire protection as the other types of coverage are distributed in other ways together with the various expenses. Fire insurance costs should be adjusted according to the schedules made up by the underwriters.

The expenses must be analyzed and charged to the departments for whose benefit they were created. Usually they are carried on the books of account under such subheadings as office, sales, administrative, general, etc. Among the expenses we also find such things as public liability, payroll and employees liability insurance. The latter is apportioned to the various departments in proportion to the dollar of payroll.

**Supplies.** — As a rule the supply items used in a manufacturing establishment are so numerous that it is difficult to account for them without getting into an expensive accounting control. The place to attack this problem is at the point of purchase. Useless purchases should be eliminated. Standardization will help to reduce the styles and types of supplies. As the greater part of the costs of supplies are due to relatively few items, proper classifications will enable us to handle many of them through expense accounts. The following list suggests useful subdivisions for the supply accounts: factory, fuel, mechanical, metered, office, packing, spare parts, and technical.

*Factory.* — Factory and packing supplies are both intimately related to current production. The items in each account should be listed, studied and standardized so that their numbers are reduced to a minimum. Factory supplies embraces such things as filter cloth, lubricating oil, steam packing, etc. Packing supplies has reference to drums, barrels, boxes, cartons, paper, twine, etc., used for shipping goods to customers. A requisition system is needed to trace the consumption of the goods controlled by these two accounts.

*Miscellaneous.* — On investigation it will usually be found that the mechanical department is responsible for more kinds of supply items than any other department. Much of this material will

add  up  to  a  relatively  small  dollars-and-cents  expenditure.
Some of the items will be found to have no characteristics which
differentiate them from factory supplies, and such articles should
be  carried  in  that  account.    A  simple  bookkeeping  method  for
handling  the. balance  of  the  supplies  used  by  the  mechanical
department is had by dividing them off into two classes, mechan-
ical expense and spare parts.    All things of the nature of re-
newal parts for machinery, etc., can be listed as spare parts and
checked  by  a  requisition  system.    A  vast  number  of  non-
descript items are easily disposed of by treating them as mechan-
ical expense later to be distributed in proportion to the hours
of activity in that department.    Office supplies and laboratory
supplies, here represented by the generic term technical supplies,
also can be handled as expenses and charged to the respective
departments at the time the materials are purchased.

*Fuel and Metered Supplies.* — Fuel, i.e. coal, cannot always be
checked  with  great  accuracy  because  weighing  facilities  are
not available and these devices are costly enough to deter many
from installing them.    A fairly satisfactory curb on coal costs
can be had by checking specific carloads of coal against power
house consumption, provided a sufficiently long period of time is
selected.    Of course, when weighing devices are available the
situation  is  simple.    Metered  supplies  has  reference  to  such
things as gas, water, and electricity bought according to meter
records from public utility companies.    If departmental sub-
meters are available, allocations can be made in accordance with
these readings, otherwise estimates of consumption must suffice.

**Labor.** — Labor has been taken as a generic term to represent
all payments of wages and salaries.    The latter, as a rule, requires
no distributions, the various amounts being charged directly to
the departments for whose account they are paid.    Labor, on
the other hand, must be followed up by the means of detailed
controls.    Common factory practice involves a time clock for
registering the *in* and *out* time making it possible to compute the
time of service in the plant.    Each week the recorded hours of
labor are extended at the various rates to obtain the payment due
each man.

Allocating labor costs to articles may require nothing further
than to charge each man's time to the department in which he
works.    In some industries it is customary to have a depart-

mental time clock so that the hours of labor spent on each detailed operation can be ascertained. When the tasks are variable as is the case with jobbing work, or when standards of performance are being developed, clocking of the separate operations is desirable. In the setting of standards such things can be carried on profitably down to the refinement of using stop watches, but after the best possible practice has been established there does not seem to be any reason why the accounting technique should be overburdened by continuing to record laboratory experiments of this character. A simple comparison between the work actually performed, extended at the standard time for the task and the total time available for such work will tell without any further frills whether or not the operations are being properly conducted. Incentive systems will do much to improve the quality and the amount of the output, provided the scheme has been thought out to a sound conclusion. Men will do a lot of things previously ignored if the proper amount of gold is visible in the balance.

**Determining Costs.** — Having determined the cost of running each department we arrive at the question of the apportionment of these values among the various unit products. There are two schools of thought on this topic. The older orthodox view contends that the *costs* should be *completely distributed to* the *output*, i.e. the products partially and completely manufactured. Newer thought gets away from this practice and merely compares the total cost for the period with the total *standard* or *goal cost* of the work performed. This subject is still so unsettled that further investigation into the merits of the two cases is desirable.

Actual costs, i.e. costs determined according to the older method, are established with the belief that once the real costs of manufacture are known, a business can be guided into profitable channels with some degree of certainty. Theoretically a solution like this to the cost problem is interesting, yet practical limitations make its application extremely difficult. This statement could be fortified with an impressive list of arguments, but only a few of them are needed to show the fallacy of the proposal. If any one believes that he can melt down in the crucible of a cost system all the diverse elements which must be bought to run a factory and from this magma produce a set of index figures, so-called actual costs, which will make him very wise let him

consider these thoughts.   The unit product costs of the modern factory are so closely tied together that we cannot determine the cost of one item without at the same time fixing the cost of every other article.   Should we abandon the production of goods which seem unprofitable we must either find a substitute for them or raise the cost of every other manufactured article. What we really need to know is the ways in which the operating elements of a factory must be handled so as to produce a desired result.   To know at all times the actual cost of every article looks like wisdom, but it does not approach it sufficiently to warrant the effort.

A clear understanding of *standard costs* is to be had by reviewing the ideas which, at some time in the past led to the erection of a given producing unit.   If the project was undertaken in the right way searching inquiries were made as to the latest manufacturing methods and as to the possibilities of profitably selling a definite amount of goods each year.   Experience has shown that we can dispose successfully of four fifths of our productive capacity.   With such basic thoughts well worked out cost accounting becomes a simple matter.   Using the four fifths capacity as a divisor we calculate a standard cost at current prices in the same terms that are used to establish the cost of running the unit.   A careful comparison between the output priced at standard cost and the operating charges leads to component differences which enable us to keep a close control on the progress of operations.   When the discrepancies are small we know that the factory is running along in the desired way and when they are large it is a simple matter to run back over the figures and find the reason therefore.   Standard costs enable us to get down to the underlying causes with the utmost dispatch and with a minimum of effort.

*Cost Standards.* — The determination of cost standards is not a difficult undertaking although extended investigations are required to get satisfactory values.   We should be willing not only to dig deeply into the subject, but also as we dig we should differentiate between the two fields of endeavor before us.   The real purpose must always be to set up the true practical situation which has been modified by the restrictions of sales possibilities and the limitations imposed by unfortunate disruptions to the continuity of operations in the factory.   Cost standards should show what can be done in an ordinary average routine way.

Another field of analysis, distinguished from routine practice, might be called the *development of correct costs*. Costs can be correct, that is, the best obtainable, in two senses. They may be correct for the process, the materials, and the factory conditions at our disposal or they may be correct for some combination of factors, not at our disposal which represent the most skillful execution of existing knowledge. Although we do not find it advisable to revise our own circumstances so as to meet the dictates of correct costs, yet full knowledge as to their real nature often enables us to guide our footsteps into more profitable directions.

Cost standards in their most useful form are divided into two parts, a *material element* and a pure *process element*. The latter must be established in those terms that are recognized in the rest of the accounting structure. The process cost standard should also be arranged so that partially completed work can be easily evaluated.

**Types of Processes.** — There are two types of processes. We have those that are used to make only one product and those that are used to make more than one product. The costs of the single product process can be calculated in terms of the finished goods, but the multi-product process must be figured in intermediate values, such as per pound of water evaporated, per pound of material ground, etc., before the costs can be allocated to individual articles. Standards of this kind, therefore, will exist without a raw material component. Sometimes improper units are selected for evaluating unit process costs. For instance the tendency in drying operations is to figure the cost per pound of material dried when the real operation is one of removing water. The correct unit is the cost per pound of water evaporated and not the more convenient value based on the residual weight of dried material.

The importance of orderly effort was touched upon in a previous paragraph. Let us examine this thought further. Even in a small business there are many transactions. Some are dealt with often and become well known, others happen rarely and are shrouded in uncertainty. For the benefit of these occasional transactions, which are members of a vast nondescript army, we must devise standard practice instructions for convenient reference whenever there is doubt as to the correct

procedure.    Should we not acquire such orderly habits we might readily find the volume of improperly handled values sufficient to seriously distort the cost picture.

**Accounting.** — Accounting is one of those sciences which is based on a few simple principles, yet proficiency in its application is not attained without diligent practice.    Anyone expecting to achieve a reasonable skill in this art without going through the tedium of constantly handling figures for an extended period might just as well shut his books at the very beginning of the subject and leave its practice to those of more patient habits. The writer, in his book "Accounting and Cost Finding for the Chemical Industries" published by the McGraw-Hill Book Company, Inc., has worked out a practical example in cost accounting.    Suggestive forms, accounts, figures, and calculations are presented to the reader, enabling him who will thread the labyrinth to grasp the interrelations between the various parts of a cost system.

Technique is of tremendous importance.    If sufficient attention is not paid to technique, the system may become very costly to run.    The standard or goal method lends itself to a simple accounting procedure.    After the initial herculean task of hewing out schedules and devising proper methods has been performed, the bookkeeping quickly adapts itself to well defined channels and produces results which are remarkably free from irritating errors.

*Service Department Costs.* — In an earlier part of this discourse the elements which fix the cost of running each department were discussed.    The total of these charges determines the cost of running the entire business for a period, but until the costs of the service departments have been reapportioned among the commercial and productive divisions, we are not in complete possession of the cost of maintaining each department.    The service departments turn out goods.    The goods which they turn out or the services which they deliver are not sold to customers, but are delivered to the production departments for use in the manufacture of the goods that constitute the trading stock of the company.    We must, therefore, measure and compare with standard or goal costs the output of each service department. The service output is charged to the production divisions on a standard cost basis according to records that are kept to show

who received the services and in what amounts. The commercial group also receives services and should be debited for the work performed for their account.

In addition to the services supplied to these two divisions, we find that there also have been activities which can be classified as *added facilities*. The mechanical department not only may have made display stands for the sale office, and repaired machinery for a producing unit; but also may have put in time on the manufacture of supplies, on the unloading of raw material, on the erection of new equipment, etc. These last three services improve our ability to manufacture and, therefore, can be called added facilities. The charges to the production departments, to the commercial departments, to the separate accounts classified as added facilities, and to the cost variations to show the differences between standard and actual costs, exhaust the expenditures made to keep the service departments running.

*Commercial Department Costs.* — The costs of the commercial departments produce a general overhead or burden of expense which cannot be reduced to unit product costs on any rational basis and being more closely related to the current revenue producing operations these charges are taken as an offset to the gross profits from sales. An analysis of the overhead burden per dollar of sales should be made. It will vary in different industries, but for a particular enterprise every effort should be made to confine these costs to desirable levels. Comparisons with the results secured in other lines often leads to constructive suggestions.

*Production Department Costs.* — The complete cost of running each production department will finally be obtained in terms of the original expenditures such as depreciation, taxes, insurance, expenses, supplies and payroll together with charges accruing from such service departments as the transportation, the mechanical, the technical, the supervision, etc. The cost of running the production departments should be compared in detail and in total with the output per department extended at standard cost and the standard cost, obviously to be of interest, must be prepared in the same identical terms as the departmental costs. The differences show how closely we are coming in practice to attaining the desired plan of action. It is difficult to properly judge an enterprise by the operations of one year and consequently these cost variations, which are based on those shorter

terms that are so essential to correct cost accounting, can serve no other purpose than to keep us constantly on our guard, anticipating serious deviations from routine practice.   If we are well informed as to the trends of a business we are always in a good position to take corrective action at a time when a very slight stimulus will be exceedingly effective.  Results do not just happen, but are realized because somebody got behind things at the right time and made them go.

A production department may make a complete article, or it may only perform a process which is one of the series of operations that are required to finish the goods in question.   In organizing these divisions it should be remembered that the point of cost focus is on the manufacturing process as an activity and not on a piece of goods.   These process costs are combined with the material costs on the books of record to get the final answer.

**Plant.** — Plant design is of great importance in cost work. Apparatus which is costly to build and costly to maintain may prove to be the most economical.   For instance by working in acid solutions one may improve the yields sufficiently to make the final costs lower even though the use of lead and brick lined equipment has increased the maintenance costs and raised the depreciation charges.   The layout of a plant may be so ill-advised that simple accounting methods for cost control cannot be installed.   Re-arrangement of the equipment should be resorted to in such cases because costs must be established if the business is to be carried on intelligently.   Often accounting will reveal that some small, apparently profitable manufacture really takes up so much administrative time and diverts sufficient attention from the volume business that, when the true general overhead cost is applied the supposed profit vanishes.

**Check on Materials.** — Making proper provisions for weighing and controlling materials is one of the essential features of plant design.   Storage space must be so located that material can be safeguarded without unduly raising the cost of putting it into process.   Yield is the backbone of the chemical manufactures. Yields cannot be exactly determined unless the input and the output of all materials are carefully checked.   From this it follows that we must have suitable weighing devices installed at strategic points, yet the passage of the goods over the scales or

through the measuring instruments must not add unduly to the cost of handling the goods.

A manufacturer buys materials, processes them and sells the finished goods to customers. In other words he enhances the value of the stock which he has purchased. Fundamentally, therefore, materials are nothing less than money and they should be checked with the same solicitous care that is our habit with the funds of the enterprise. A closely watched warehouse is of as much importance to a factory as a vault is to a bank. The goods are checked on arrival; are issued only on a written order; are again checked at the time of disbursement and the balances on hand are verified at convenient intervals. This practice is essential, not only to cost work, but also to the successful conduct of an enterprise. Loose habits lead neither to knowledge of costs nor to profits.

From the viewpoint of control, a factory has to deal with two kinds of materials. There are those which can be definitely identified at all times and those whose identity is lost after they are mingled with other goods of the same kind. In illustration of the first class we have all package goods or articles that can be serially numbered in some positive manner. Materials packed in barrels, etc., however, join the second class after the container has been opened. The only way the disbursement of bulk goods can be checked is by isolating a lot or shipment until all the goods have been used and at that time verifying that the theoretical book balance also shows nothing on hand. If small lots are dispensed from bulk goods the sum of the weights of the separate parts will always be greater or smaller than the original total. This is due to the cumulative effect of the inaccuracies in individual measurements. Experience finally enables us to set up an index figure which shows the normal error for a given raw material.

*Warehouse Records.* — Warehouse records should be kept in books of the loose leaf type, with rigid post binders and not on cards, for with the latter we are only too apt to lose or misplace vital statistics. Nothing more than quantitative facts need be entered. Dollars and cents values can be established whenever an inventory is taken. To inject such information into a warehouse record tends to make us lose sight of the real purpose of the stock sheets, namely to tell the quantity of goods on hand.

With bulk goods the quantity of material received is entered on the left hand side of the page and the amount disbursed on the right hand side. A middle column provides a place for entering the balance on hand at such times as this value is calculated. Dates, identifying numerals, names of the shippers and names of the users are also placed on the records.

For goods which can be identified after being placed in stock, a slightly different procedure is followed. Instead of merely entering the total amount of the shipment on the left hand side of the page, each separate item with its identifying marks is posted. Whereas before the withdrawals were listed consecutively on the right hand side, now the releases are noted on the same horizontal line with the original entry showing the receipt of the particular item in question. To get the balance on hand it is now necessary to run back over the records and list up on an adding machine the lots which have not been marked as disbursed. The great advantage of this method, where it can be used, is that it shows the exact manufacture in which each item was consumed. In the chemical industries where the quality of the raw materials plays so important a part in producing consistent results, we should be able to check back and reestablish the purity of our materials.

A written order, or requisition as it is usually called, is issued to authorize the removal of goods from the warehouse. Frequently people try to make this voucher show what was done with the goods when really all that this document can do is to attest the delivery of goods to a particular department. To get an exact check on the stock put into process it is necessary for each department to keep a set of records similar to those of the warehouse. A blackboard or small memorandum book will usually serve this purpose. The factory and warehouse stock sheets must be checked against each other if our material control system is to be rigid and leave no loopholes for the loss of goods.

*Raw Stock and Partly Manufactured Stock.* — There are a few salient points which must be kept in mind while we are studying the control of materials in the factory. When a given quantity of goods is manufactured, the amount of raw material required for this purpose may be either fixed or variable. An assembly operation will require the same number of parts, rivets, etc., for each unit made up, but the neutralization of a batch of chemicals will not always take the same identical amount of acid. To

control the materials used in the first type of work we need only know the number of units made up and extend this amount by a standard bill of materials. This simple method gives us the consumption of goods when their use is fixed. Under variable conditions, however, factory notes are needed to establish these statistics.

In the chemical industries it is common practice to enter the field notes in a columnar book. A separate horizontal line is used for each batch or lot made up and a separate vertical column is devoted to each raw material consumed in the manufacture. By footing up the columns we can quickly get at the amount of each chemical employed in the production of a series of batches. Yields of finished goods are usually also entered in the same book. This record is well suited for running down average values and such other facts as the chemist must know. If these statistics are carefully checked against warehouse figures we have an excellent original entry book for cost work.

Some materials are used entirely for the production of a single article; but others are used in the same department to make various products. Checking the stock employed under the first conditions is not difficult. Where more than one article is made from a given material its consumption must be apportioned among the various members of the group. There are two kinds of these groups. One gives rise to so-called class products and the other to joint products.

Class products differ from joint products in that we can use selective powers in picking members of groups of the first type, whereas in the second case, for an accepted process the combinations are completely determined by the characteristics of the material itself. For instance in the sulphonation of an organic compound yielding two products A and B, by varying the conditions of the sulphonation you can produce a melt containing mainly A or B; but as soon as the conditions of the manufacture are fixed the two joint products, A and B, are obtained in the same proportion in every batch. On the other hand if one is making castings he can produce at will harness hooks, door knobs or any other set of articles for which he has orders. Goods which are grouped together merely because they happen to be made from one lot of raw material are called class products.

There are three wyas in which a material may be used by a department to make more than one article. First we have the

case of the rotation of production, necessitating a check as to the quantities of raw material used in the consecutive manufacture of a number of articles related in no other way than that they are all made by one department.  Second with class products a given amount of raw material must be apportioned to each member according to weight or some other unit of measurement, because the manufacture of the group exhausts the allotted supply of material.  Third, with joint products the distribution is done empirically, each member of the family being called upon to bring in as much of the total cost of the material and process changes as he can command in the market place.

The control of materials by the methods described in the preceding paragraphs is known as the perpetual inventory system because we are able at all times to find the stock on hand if we want to go to the trouble of balancing the receipts and disbursements.  It should always be borne in mind that material records are kept so that a check on the use of goods can be made. If the work is done accurately, then the true inventory on hand will lie within the books even though it has not been brought to the surface as an actual entry.  Contrast these methods to those of the past when goods were brought, used and the finished articles sold to customers without any office control other than to go through the factory once a year with the hope that a physical count would give the exact amount of unconsumed stock on hand.

The dividing line between supplies and raw materials is not always well defined.  The differences between the two groups lie in that supplies are articles which we use in an indirect way to help us produce saleable goods, whereas raw materials are goods which through process changes are converted into new articles.  When we come to the chemical industries with their catalytic agents these boundaries must be defined in a little different way.  We are led to view as raw materials all goods whose consumption varies in proportion to the production of finished stock, provided their contribution to the cost picture is sufficient to warrant the expense of the more rigid material controls.  It should not be overlooked, however, that some supply items are so costly that an extremely close check on their consumption is required.

*Stock Accounts.* — A number of ledger accounts have become well established as controlling agencies for materials during their

progressive passage through the factory. When goods are bought they are charged to a *Raw Material Purchase* account, which at monthly intervals is transferred to another account called *Raw Materials*. This procedure gives a little clearer picture of the actual events in that we are able at all times to check the total amount of goods bought together with any credits for returned or defective materials without wading through a mass of unrelated figures pertaining to the inventories on hand and the amounts of goods put into process.

Stock withdrawn for manufacturing purposes is deducted from the account *Raw Material* and charged to *Work in Process*. The cost of process changes, i.e. related departmental activities, is also posted to the account *Work in Process*. Completed articles are credited to this account and the balance left in the account at any time reflects the inventory of uncompleted work. After the goods are finished they are charged either to a *Component Materials* or a *Finished Stock* account, depending on whether the articles are ready for the market or need further processing before they can be sold.

A classification intermediate to work in process and finished stock makes it possible to come to a conclusion with the cost calculations at an early period. If the accounts in a standard cost system are not cleared promptly large cost variations are apt to accumulate causing the inventories to reflect anything but the true state of affairs. The outstanding advantage of the goal or standard cost method is that it enables you to develop a technique which makes the prompt delivery of cost data the natural thing to do.

No profits should be incorporated with the inventory values· of component materials because that would violate an accounting principle which says that we should not anticipate profits. The margin on which the final goods are handled should allow for a profit on the processing of the intermediate or component parts.

It can be accepted as a general principle that output values of goods from a department should not be used in the cost calculations until these figures have been verified by a warehouse count. There are instances where it is not possible, except at great cost, to place finished items in stock, yet when this cannot be done, then a check by an inspector should be used in a manner giving the equivalent of a warehouse control. At monthly

intervals all articles sold are credited to the account *Finished Stock* and charged at cost to an account called *Cost of Goods Sold.*

**Evaluating a Business.** — *The Balance Sheet.* — The quickest way of getting a real insight into the business side of an enterprise is by studying the source of its income and by analyzing the nature of its expenditures. The balance sheet is the proper starting point for an investigation of this character. This accounting statement shows the values which were owned by the business and the obligations which were owed by it to others at the particular moment when the balance sheet was made up. In other words it gives a picture of the values existing at a given instant.

If we strip a balance sheet down to the basic facts and ignore such items as the little adjustments which the accountant must make to allow for prepaid insurance, taxes and similar things we arrive at the following exposition of values:

ASSETS

Current { Cash
          Receivables
          Inventories

Fixed    Real Estate
         Plant

LIABILITIES

Current { Payables
Long Term { Bonded Indebtedness
Owners Shares { Capital
                Surplus
                Profit for last period

The inquiry should first be directed towards the ratios which exist between the various members of the balance sheet. In a healthy business these should compare favorably with the values that are considered normal for the industry under consideration. J. H. Bliss has written a book "Financial and Operating Ratios in Management," published by the Ronald Press Company, which can be consulted profitably by those in search of more detailed information on this subject.

The important thing to examine on the balance sheet is the amount of working capital, i.e. the difference between the current assets and the current liabilities. This is the fuel that keeps the business fires burning. Successful management requires us to go down deeper into these values and compels us to keep a watchful eye on the quick liquid assets of the enterprise. Inventories are usually taken as current assets, but at times, for an extended period, the stock on hand may be quite unsaleable. The market may be glutted with goods or for extraordinary reasons the consumption of certain articles may have fallen to low levels. The trade is accustomed to doing things in a routine manner and when we precipitate such excitement as trying to move an unusual amount of goods chaotic conditions are apt to ensue. Some of the accounts receivable may not be due, yet if the obligations have been contracted for by a reputable concern such assets are among the best for borrowing purposes. If, therefore, we deduct the inventories from the working capital we obtain the quick liquid assets and it is on the components of this sum that we must depend for the more sudden changes in our plan of financial management.

**Financial Trend of a Business.** — A business is not a thing that can be turned inside out in a hurry, but is rather a thing that has to be slowly guided into the new direction which you wish it to take. An enviable reputation for promptly meeting all current obligations is a great asset to a business, yet sudden shifts in fundamental conditions may make it difficult for us to pay our bills on time. Quick liquid assets are so helpful in meeting the unexpected turns of life that we cannot give too much attention to them in business management.

Figure 164 shows a graphic chart which is well adapted to the control of accounts receivable, accounts payable, cash, and the difference between these values, known as the *Net Balance*. The various sums are plotted according to the usual graphic methods, using a yearly sheet on which there is a line for each day. Colored crayons make the diagram easier to follow. Short term notes, i.e. four months borrowings from the banks, are considered as accounts payable; similarly trade acceptances and equivalent instruments are considered as accounts receivable. By reducing purchases, by accelerating sales, or by stimulating collections the heavy black line, *Net Balance*, can be kept at

those levels which are found desirable under a sound policy of management.

Whereas the balance sheet shows the values which exist in a business at a particular moment, the income, profit and loss
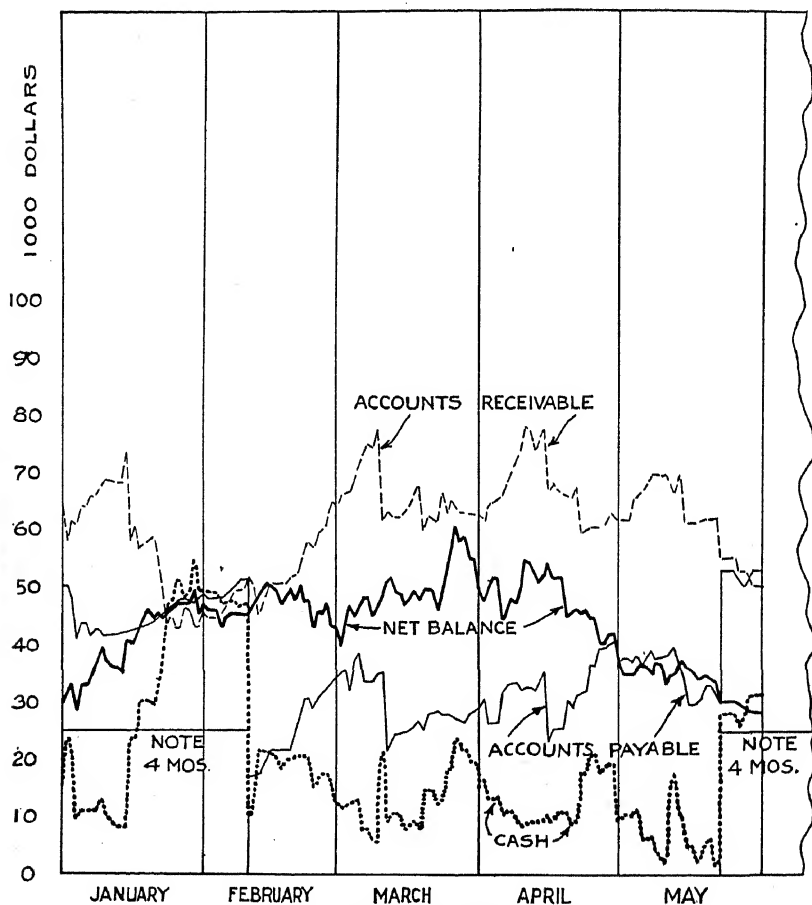


FIG. 164.   Financial Trend Chart.

statement shows the forces that produced the changes which occurred since the last balance sheet was taken. Today the published profit and loss statements of corporations are becoming conspicuous for their brevity. This is a step in the right direction, but unfortunately the tendency is to omit the supporting

schedules without which the profit and loss statement becomes a meaningless tangle of figures. Often we merely find listed the gross profit from sales, the miscellaneous income, the operating costs as a lump sum, the Federal taxes and similar items. Such facts give only a sketchy outline and do not permit us to arrive at the true underlying situation. To get the complete story we must scrutinize such things as:

A. The sales,
B. The cost of the goods sold,
C. The cost of the goods manufactured,
D. The cost of the raw material consumed,
E. The departmental cost elements,
F. Departmental costs,
G. Process costs,
H. Cost variations or departures from standard practice.

That an enterprise must be carefully guided becomes apparent when we scrutinize the five most common causes of failure in business.

1. Profits insufficient,
2. Inventories overextended,
3. Accounts receivable overextended,
4. Fixed asset investment too great,
5. Capital insufficient.

Not the exact evaluation of past activities, but a solicitous directing towards the results that should be attained is the keynote of costs and financing. Only by planning, planning, planning are factory operations conducted with the greatest success. Prominent among the things which must be provided for against a future need are the raw and finished goods of the manufacturing industries. Goods are often obtained most economically from distant points and to have them on time we must anticipate consumption. Again when orders are placed customers want immediate shipment and not promises of a future delivery. By careful planning we can have goods on the shelf ready to pack even in some of those trying moments when erratic demands are made.

Figure 165 suggests a convenient graphic method for controlling materials so as to meet future requirements. Both the production and the sales lines are cumulative for a three months period.

The difference between the two graphs, at all times, depicts the warehouse and in process inventory of goods. The sloping lines show the relation between the actual sales and the estimated quota for the period. Columns of figures are inferior to the
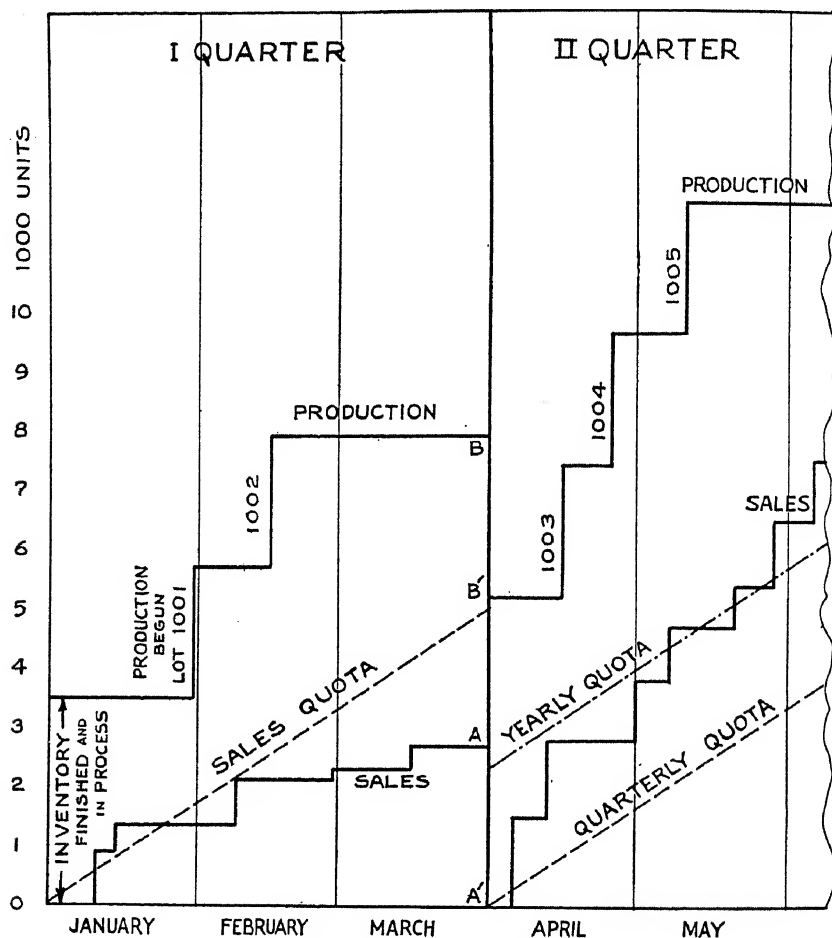


FIG. 165.   Production Sales Chart.

graphic method because they do not enable us to visualize trends in the same clear way. A record of this kind for each important raw material and finished article is of inestimable value in planning future activities.

If we really understand what might be called the structural details of factory costs we naturally fall into the habit of budgeting. Intimate knowledge not of article costs, but of the way the purchased elements fit together to produce a desired result brings the realization that the payroll must harmonize with the sales, that a given payroll demands a definite amount of raw material for conversion into finished stock, and that all the other expenses of a business cannot be allowed to exceed certain values without destroying the profitable balance of the enterprise.

### PROBLEMS

70. If the cost of a machine is $1500 and it is depreciated at the rate of 10 per cent per annum, what is the amount of depreciation to be taken in the fifth year by (a) the straight line method and (b) the method of diminishing balances.

71. The Transportation Department of a corporation, on its monthly labor report showed 397 hours spent in taking material out of the warehouse for use in production; 431 hours spent in delivering finished goods at the freight terminal to be shipped to customers; 125 hours spent in unloading coal; and 305 hours spent in carting construction material for a new plant unit being erected. At the rate of 40 cents per hour what are the charges which should be made and to what accounts should they be debited?

72. The unit standard or goal cost for processing in Production Department A is: Depreciation $0.75; Taxes and Insurance $0.16; Supplies $0.06; Fuel $0.10; Payroll $4.15; Real Estate Service $0.30; Labor Overhead $0.20; Transportation Service $0.05; Mechanical Service $0.05; Steam $0.75; Electricity $0.45; Technical Service $0.08; and Supervision $0.22. The total standard processing cost for Production Department A is $7.32. During the month 1028 units were processed. The cost of operating the department was as follows: Depreciation $750.63; Taxes and Insurance $163.59; Supplies $55.85; Fuel $98.18; Payroll $4378.90; Real Estate Service $287.50; Labor Overhead $197.05; Transportation Service $50.60; Mechanical Service $64.90; Steam $785.00; Electricity $422.16; Technical Service $90.00; Supervision $232.79; and Total Cost $7577.15. By how much did the standard or goal cost overreach or fall short of the actual cost of running the department? Also give the nature and size of the cost variation for each element of departmental cost.

73. The first cost of a manufacturing unit is $272,000. It has a capacity of 60 tons of finished product per day. Operating 360 days per year, what is the investment per annual ton of finished product.

74. The total standard cost, raw material and processing, for a given finished item is $1.62 per unit. The total cost for producing 3000 units charged to the Work-In-Process Cost Sheet is $4942.94. In the course of this manufacturing operation 450 units of a by-product with a market value of $0.30 per unit are produced. What is the cost variation when the yield of finished product is as anticipated? What is the cost variation when the yield falls to 90 per cent of the desired amount? What is the cost variation when the yield rises to 110 per cent of the standard amount?

75. The balance sheet of a corporation reads as follows:

### Assets

| | |
|---|---:|
| Cash | $ 47,458.48 |
| Accounts Receivable | 78,720.12 |
| Prepaid Items | 5,947.70 |
| Inventories | 189,474.64 |
| Land, Buildings, and Plant (depreciated) | 405,609.71 |
| Total Assets | $727,210.65 |

### Liabilities

| | |
|---|---:|
| Accounts Payable | $ 35,840.16 |
| Accrued Items | 1,700.66 |
| Capital Stock | 500,000.00 |
| Surplus | 189,669.83 |
| Total Liabilities | $727,210.65 |

The gross sales for the past year were $1,237,649.99. Assuming twelve 30 day periods to the year, how many days of sales are tied up in (a) inventories, (b) in Accounts Payable, (c) in Accounts Receivable? What is the ratio of current assets to current liabilities? What is the ratio of quick assets to current liabilities?

# CHAPTER XVI

## PLANT LOCATION

### J. L. WARNER, B.S., C.E.

The experience gained by manufacturers in the past thirty years has established the fact that the scientific location of a plant plays a large part in the successful operation of that plant. In our grandfather's time a mill was built by a stream of water and people came to the mill; in our father's day the market was the determining element and the factory was located near its market. During the last generation the United States has started to change from an agricultural country to an industrial nation; our industrial life has become so complex that the simplicity of our forefather's day is a thing of the past. Years ago the selection of a site did not require much scientific study. Water power may have been the main consideration, transportation systems were relatively crude and markets were small and near at hand. Practically no business was large in the present day sense, and the entire industrial structure was localized and simple. Today, however, with business on such a vastly larger scale, every item entering into the large investment and operating costs of a plant must be scientifically studied and weighed if that plant is to remain successful in spite of the keenest competition.

In traveling about the country one frequently sees abandoned factories, having windows boarded up and rusty smokestacks with "For Sale" signs displayed. The question naturally arises "Why were these plants not successful?" A study of the history of such plants would probably point to one of two major cases: absorption of small individual concerns by large corporations (with which we are not concerned in this chapter) or the violation of the fundamental principles of good location.

**Fundamentals of Plant Location.** — The fundamental principles of plant location can be expressed in one word, *costs*, and costs only. However, this item, *costs*, must be interpreted in the broadest sense of the word. It involves not only a consideration

of immediate costs but costs which may arise throughout the future life of the plant.   In some instances it may include the selection of a site which will best meet present and future competition; in other instances it may include the avoidance of locations near competitors, where the interchange of employes may be the means of carrying valuable process secrets to other concerns, so that in this broad sense "costs" is not just one of the important items, it is the only item to be considered.

It may be aesthetic to locate a plant in a setting of beautiful mountain scenery or on a high bluff overlooking a lake.   It may appeal to a few, even in authority, to have their company's plant located in their home town or where the climate and living conditions for them are ideal, regardless of the cost of putting it there and the high costs of operating the plant in that location. However, the location of a plant is purely business (dollars and cents) and the most successful location is that place where the total of all the *costs* of building and operating the plant is the lowest.

Costs are divided into *investment* (or initial) *costs* and *operating costs*.

*Investment Costs*. — Investment costs may be defined as those charges accruing prior to and during the actual building of a plant.   Operating costs are those continuous expenses resulting from the manufacture of the commodity which the plant was built to produce.

Initial cost represents the actual investment in physical property and includes all the items of expense from the engineer's investigation, design and location, on through the purchase of real estate and the actual construction of the plant, equipped and ready for operation.   The sum total of all these charges must be regarded in the light of money borrowed at the prevailing rate of interest.   The interest charge on the capital investment will be referred to later.

*Operating  Costs*. — Operating  cost  represents  the  cost  to produce the plant's commodity, including purchase and transportation of raw materials, the conversion of the raw materials into the finished product, the shipping, storing and distribution of the finished product, and the maintenance and overhead of the plant itself.

The unit production cost is all of the operating expenses during any period divided by the quantity of finished product produced

during that same period. When the site is located, the plant built and operation begun, the investment cost is included in the operating cost as an overhead expense in the form of "Interest on Investment." The unit cost must be kept at the lowest possible figure. Much has been accomplished in recent years in improving the efficiency of plant operations, but once a plant is located, any inherent faults of location are forever carried on as a burden by the manufacturing plant. Operating faults can very often be corrected or improved at comparatively little cost but once a large investment for a plant is made, location faults may only be corrected by incurring an enormous expense. Thus it will be seen that *investment costs*, as well as *operating costs*, constitute the unit cost of the finished product and, therefore, the proper location of a plant is vital, for upon this one phase alone the future success of the plant is very apt to depend.

It would not be possible to prepare a list or chart showing all of the items which, under any circumstance, might enter into and make up the investment and operating costs. The accompanying Fig. 166 is only intended to give a general idea of the scope of these two classifications.

**Factors of Site Selection.** — In considering the factors of site selection, the foregoing analysis of the fundamentals of plant location should be clearly kept in mind. First, scientific study is necessary because of the very complex nature of our present industrial structure; second, though having many ramifications, costs in their final analysis are, or certainly should be, the one and only basis on which a site for a proposed plant is chosen.

The procedure followed in the selection of the site is made up of several very definite steps, each step logically following the preceding one and working down to the final goal — the actual choice of the site. These steps are:

1. General plant requirements, or the given specifications.
2. Relation of specific to fundamental requirements.
3. General scope of investigation.
4. Narrowing the field.
5. Specific geographic locations.
6. Preliminary field studies — obtaining data.
7. Preliminary report and further narrowing of field.
8. Cost study — specific locations.
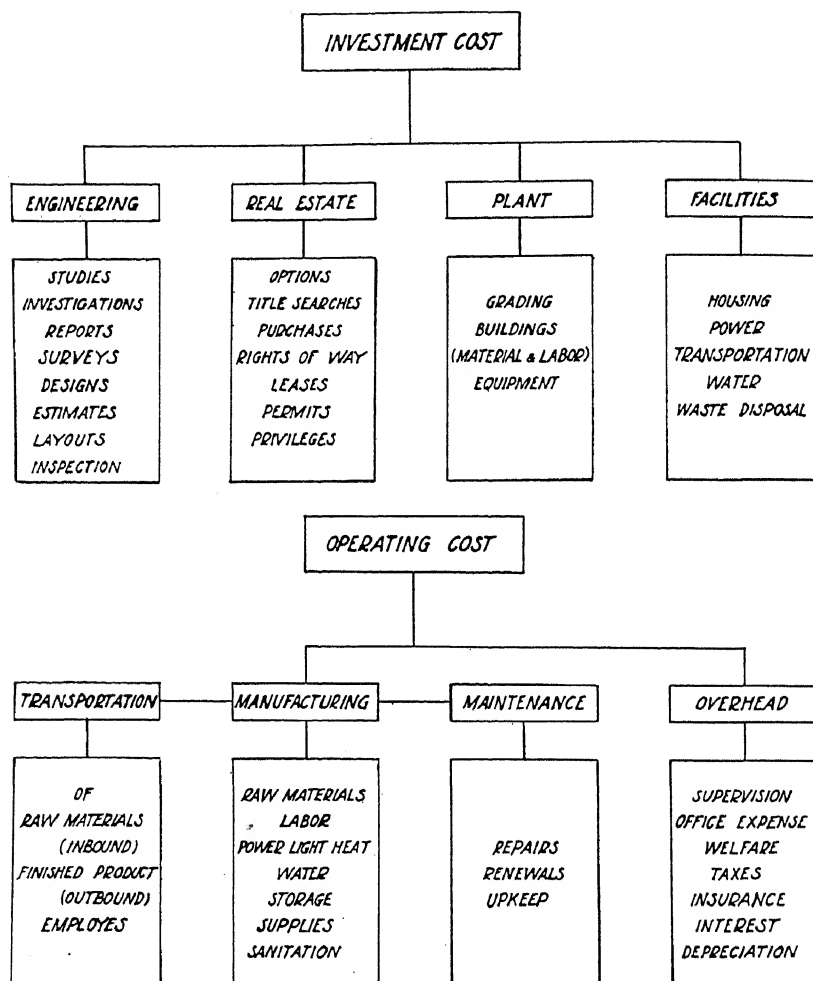
$$\frac{OPERATING \quad COST}{QUANTITY \quad PRODUCED} = UNIT \; PRODUCTION \; COST$$

Fig. 166.   Investment and Operating Costs.

9. Selection of a few outstanding sites.
10. Real estate and property options.
11. Detailed studies:
     Sites,
     Proving preliminary investigations,
     Costs — investment and operating.
12. Selection of the site.

It will be noted from the steps followed that in the very earliest stages, from the plant location engineer's viewpoint, it is only known that a plant location is desired and that he may have an entire country, if not the entire world, in which to finally choose the site. From the developments of each step his problem is one of progressively narrowing the field until the one final location is selected.

Of course, the size of an industry, the scope of that industry's business, the markets, the general requirements and many other considerations may immediately bring about such a sudden reduction of the territory to be considered, that many of the above steps are at once eliminated. This will be especially true in the case of a small industry contemplating a small plant and intending to serve a particularly localized market. For instance, a Pennsylvania lumber concern desires to enter into the mine prop business and supply the coal companies in the anthracite field. Owing to the nature of the business and the localized market, the field becomes immediately narrowed down to, say, the northeastern section of Pennsylvania. After investigating timber lands, costs of sites, saw mills, labor, transportation, etc., the field may again be very quickly narrowed to a few sites from which the most favorable one is selected. As a general rule, the larger the business, plant, market, etc., the greater the number of steps to be taken and hence the greater the problem of site selection. These steps will now be taken up separately.

*1. General Plant Requirements.* — The general plant requirements are the first specifications that the plant location engineer receives from the officials of his company. If the nature of two proposed plants is entirely different, then the specifications will probably be entirely different and the engineer must govern himself according to the specific problem in hand. Even with two plants making the same product, the specifications may vary considerably. In this case, though the same product is made,

the process may not be the same, a different market may have to be supplied, a different means of transportation of raw materials or finished product may loom up, a new source of raw materials may have to be considered and in fact innumerable conditions may arise which will vary the general requirements of even two plants making the same product.

When a new plant location is being first considered, the plant location engineer should be at once taken into the confidence of the officials of the company.  It is at these preliminary discussions that he obtains the broad view of the executive and hears the reasons for the development of the general and specific requirements.  Having heard these discussions first hand, the engineer is then in the best position to carry out the wishes of the officials of his company throughout the many details of his investigation.  Furthermore, at these preliminary discussions, he is often able to offer valuable suggestions and raise questions in regard to the major requirements which will effect large savings in the cost of the site investigation.

The following list of general requirements is not intended to be exhaustive — covering all types of plants under every condition and circumstance.  The list is only intended to represent some of the main items that would be covered in general requirements; in fact the specifications received by the plant location engineer may be very broad and not nearly as complete as the following list. Each problem will have certain specifications peculiar to it but, in general, several of the following items may be expected to be given or immediately developed by the engineer from the data first received.

*A. The Plant*
> (*a*) The product or products proposed to be manufactured.
> (*b*) The proposed capacity — initial and ultimate.
> (*c*) The approximate initial and ultimate dimensions of
>> (1) One building if all under one roof.
>> (2) Various buildings if the manufacturing process demands it.

*B. Locations*
> As determined by requirements pertaining to:
> (*a*) Markets desired to reach.
> (*b*) Probable or possible raw material sources.
> (*c*) Industrial village contemplated or not.

*C. Land*
> (*a*) Approximate total acreage desired.
> (*b*) General nature of topography desired.
> (*c*) Unusual bearing values of soil desired.

D. *Labor*

    (*a*) Immediate and ultimate number of employes, male and female.

    (*b*) Type of employes — skilled or unskilled.

E. *Power*

    (*a*) Kind of power preferred — electric, water, steam.

    (*b*) Amount of power desired.

F. *Water*

    (*a*) Quantity of water — immediate and ultimate.

    (*b*) Quality of water desired — chemical features, physical properties, temperature, etc.

G. *Waste Disposal.*

    (*a*) Quantity of industrial waste.

    (*b*) Nature of waste — solid and liquid, fumes, odors, smoke — objectionable and unobjectionable features.

*2. Relation of Specific to Fundamental Requirements.* — It would not be possible to cover all of the ways in which the general plant requirements are related to the fundamental factors of plant location. Each location study will bear its particular relation to these fundamentals which must be ever present in the mind of the engineer. Some of the ways in which a study may be related to the fundamentals (costs) of location will be discussed.

*A. The Plant.* — A knowledge of the general nature of the location desired can only be obtained from the type, kind and size of plant being considered. If the plant is to consist of only one relatively small building, even though several stories in height, then as far as the building is concerned almost any location would do. Since the area to be occupied in this case is relatively small, the cost of the site will depend on its location with respect to heavily populated districts. In the heart of a large city the cost of the site may be high but if the plant can be just as well located outside city limits, the cost of the site will be apt to be less and less significant as the distance from the city is increased.

*B. Locations.* — In many instances the general requirements as to markets to be reached, sources of raw materials, proximity to centers of population, etc., will lead to a preference for a specific location of the proposed plant. However, if the raw materials and finished products are relatively light in weight, it may be found that transportation costs are a relatively small part of the

unit cost of the finished product. In such a case the nearness to raw materials and markets may be comparatively unimportant. Conversely, it is evident that these two factors may be vital and almost entirely control the location of the proposed plant. Again, in one instance an industrial village may be absolutely necessary while in another case it is to be avoided and the plant located near a large town or city.

An industrial organization is not equipped to take up civic duties. When it is necessary to build a large industrial village it does not end with the building of the houses. Churches and schools must be built; various stores must be constructed, equipped and operated; streets, sewers, water supplies, meeting halls, amusements and countless other things must be provided. The community's political development takes place and the company finds itself forced to enter into even this phase of life. So in many ways the company building an industrial village adds a large and unnatural burden to its many problems and, wherever at all possible, the responsibility of housing employes should be avoided.

C. *Land.* — The total area required will have a direct relation to the cost of the site. Here again the proximity to the centers of population will, as a rule, increase the cost of land per acre or per front foot, depending on the unit in which the land is dealt. The nature of the business, the kind and size of buildings and the relation of the buildings in the operation of the plant will generally determine the desired topography of the site. All requirements must be thought of in terms of fundamentals — costs. If the plant building or buildings are relatively large, flat areas are obviously desired so that heavy expenses of grading a site may be avoided. If the buildings are relatively small and the nature of the plant's operations do not require them to be on the same level, it is apparent that rolling or slightly hilly country may be selected. In some cases, as for instance, the explosive industry, a site in hilly country may not only be desired, but will be demanded, to afford natural protection for various operations which would otherwise have to be provided at a considerable expense. Generally speaking, sites of a rolling or hilly nature are less expensive than the more nearly level sites. Land which is fairly level is as a rule used for high grade farms or held for real estate developments. Some meadow or low lands may at first appear to be cheap as far as the actual price per acre is

concerned but here again other factors must be considered. Though a meadow land may be cheap, it may be swampy and the bearing value of the soil may be entirely inadequate for the particular plant under consideration. Furthermore, the meadow land may be subject to frequent flooding which would seriously handicap, if not totally destroy, the value of the site as a place to construct and operate a plant. In other words the selection of meadow land, because of its apparent advantage of being flat and relatively cheap, may incur far more serious disadvantage through flooding and the necessity of driving piling for all foundations. It will be seen that not only one cost but all costs must be weighed by the plant location engineer.

*D. Labor.* — Labor costs must be thought of in connection with the plant construction (investment costs) and especially considered in connection with plant operation (operating costs). For, after all, the construction of the plant is only a part of the fixed initial cost whereas the plant operation may be expected to continue for years and these operating costs vitally affect the cost of the finished product in time to come. The relative importance of labor costs can be visualized from the nature of the proposed industry, and the number and type of workers to be employed. Obviously, with other conditions nearly equal, a location where industrial workers are contented and satisfied will always be preferred to a location where discontent, strikes and various kinds of labor troubles are to be anticipated. The very nature of some industries will indicate that labor cost is one of the main, if not the greatest, single item affecting the unit cost of the finished product. Almost invariably the officials of a company will know to what extent labor rates affect the costs of the finished product. When labor rates are vital, the engineer will be led to give first consideration to those general territories or sections of a country where labor and industrial wage rates are low. Great care must be exercised to avoid being unduly attracted by purely low wage rates. The engineer dare not be content with only the knowledge that the wage rate of a certain section is low, but he must know exactly why it is low. Wage rates may be low because of an inferior class of help or they may be only temporarily low in a certain territory because the supply far exceeds the demand. The engineer must be certain that these are not the prime causes for the low rates in the area under investigation for it is exactly these conditions he must avoid.

He must be assured that there are certain inherent reasons for the low rates, that the workers are not inferior and that, regardless of the fluctuation in industrial rates throughout the country as a whole, the rates in this particular section will always be lower. There are always certain sections of any country where these lower rates exist because the favorable temperature, climate and general living conditions permit a good standard of living at less expense than in other climates. In other words, the best quality of workers and the lowest rates are generally found where the temperature is warm or mild and the climate is pleasant and healthful the year round. In these locations houses are cheaper as no cellars are required and heavy protection against the elements is unnecessary; living costs are less as no artificial heat is required and uniform weights of clothing may be worn by all throughout the year. It will also be found that living costs are higher in cities than in suburban and country districts.

Then again an industry may require skilled workers of a particular type and this may lead toward the first consideration of those sections of a country where there is an abundance of this class of help. For instance, in the United States, Detroit is famous for its automobile industries and mechanics of this type may be found there in abundance. Similarly, Akron, Ohio, for rubber industries; New England for brass and machine work and other localities where the workers are very skillful along highly specialized lines. Therefore, cases may arise where it may be more profitable to locate in a section where the particular type of employes can be obtained at once and the expense of training and loss of time in developing these workers can be avoided.

*E. Power.* — Here again the nature of the industry, the kind and amount of power desired and the extent to which power costs affect the unit cost of the finished product will tend to direct the engineer toward the best solution of this phase of his problem. The relation of this or any other major requirement can only be determined in the light of its effect on the final unit cost of the product. In the reduction of aluminum from the ore, cheap power is the most important consideration, whereas in some other industry power may be relatively insignificant. Where abundant water power is available, electric power will be relatively cheap, and for the same reason in territories where steam coal prices are low, both cheap steam and electric power can be anticipated. Electric power is being used more and more, and

with the rapid development of public utility companies, cheaper electric power is extended to all sections of the country through the vast net-work of high tension transmission lines. Even so, it costs money to transport power whether it is electricity through transmission lines or coal in cars along a railroad. Some sections will always have cheaper power than other sections because of varying natural advantages.

The engineer dare not be satisfied with any single rate quoted by a power company. At the present time most companies have regular fixed published rate schedules or tariffs. These rates are almost invariably on a sliding scale, depending on the quantity of power to be consumed in a given time and the maximum demand to be made at any one period during a day, week or month. The relative cost of electric power with various tariffs can only be determined by applying the power requirements for each particular case to each entire schedule.

Though a plant may originally contemplate purchasing steam power the engineer should know the kinds and costs of various coals, as it may be cheaper for the company to make its own steam and this situation may be forced upon them at any time. It is not sufficient to know only the price per ton of coal, but in each case the engineer must have the detailed analysis of the coal as some fuel is cheap because it is low in heat units whereas a higher priced coal may be far cheaper when considered in terms of its heat producing values.

In large plants enormous savings in power costs can very often be effected by a study of the heat balance for that particular plant. To explain this term more fully, the process of a plant may require a large amount of low pressure steam as well as a considerable amount of electric power. To generate the electric power in the first place may require a large amount of high pressure steam, which, after passing through the turbines, is usually taken to condensers at a considerable loss of heat. If there exists a sufficient balance between the high pressure (high temperature) heat required and the low pressure (low temperature) heat needed in the process, large economies can often be effected by the more efficient use of these heats. In other words, instead of purchasing electricity and making low pressure steam for process purposes, the plant may be more than justified in making their own electric power, passing the high pressure steam through the turbines and utilizing the exhaust low pressure

steam for manufacturing purposes. In this way, electric power for the plant may be had at only a fraction of the best purchase price obtainable.

*F. Water.* — Water is often one of the controlling factors in the selection of a site. The engineer must know the bacteriological as well as the chemical analysis of the available supplies, the quantities available from lakes, streams, rivers and wells and the temperatures and physical properties of all water sources. At least a small source of pure uncontaminated water will be desired for drinking purposes or the water must be filtered and treated for this use. The chemical content of the water used for industrial purposes may be of vital concern to the process of manufacture. The presence of some minerals in solution may discolor and ruin the finished product. The question may naturally arise " Cannot these objectionable features be counteracted or removed by treatment?" The answer may often be "Yes" but the process of treatment may be so expensive that the cost of water of the right kind becomes abnormally high, and throughout the entire investigation the engineer must never lose sight of the fact that the fundamentals of plant location revolve about one consideration — Costs.

In certain general areas waters will be found to possess the characteristics of that area. In regions where coal and iron mines predominate the waters will be apt to be high in iron. In certain areas where limestone predominates, the waters will be apt to be hard. In some areas, underground waters may be particularly cold, while in other areas the temperature may be very high. Often the engineer receives data on the "Average minimum flow" of streams. This information may serve some purposes but is of little value in this form to the engineer selecting a site for a plant. Most plants contemplate operating eight hours per day if not 16 or 24 hours per day, so that the absolute minimum quantity of water which can be expected from any source must be known, even though that minimum may only exist for a very short period of time. The shut down of a plant for lack of water for even an hour may cause considerable damage and expense.

*G. Waste Disposal.* — The disposal of industrial wastes is constantly becoming more and more difficult. Years ago an industry could dump almost any waste into any stream. However, with our ever-increasing population, towns and cities are

building up along streams and lakes and constantly demanding greater amounts of unpolluted water. Health authorities generally are requiring new industries to treat their wastes before discharging them into public water courses and though the engineer may find that a certain locality does not require new industries to treat their wastes, nevertheless no company should expect that this condition will always prevail. For this reason the engineer will obtain all data possible relative to the future requirements for the treatment of wastes. Furthermore, gases and fumes in connection with the prevailing direction of the wind must not be overlooked.

3. *General Scope of Investigation.* — From the foregoing it is apparent that when the plant location engineer correlates all of the general plant requirements with the fundamentals of plant location (costs), his problem at best is a most intricate one. In the first place he must realize that he cannot possibly find one location which will be ideally suited to all requirements. The reason for this is that in some respects, if not many, the requirements themselves are conflicting. For instance the demand may be for a large supply of good labor at low rates and at the same time a demand for cold water. The lower wage rates are to be found in the more uniformly warm climates whereas the cold water will be found in the colder climates. Again, the requirements may demand proximity to raw materials and also to the markets and these locations may be widely divergent, making it physically impossible to fulfill both demands. And so on, in innumerable ways, the general plant requirements may conflict, making it impossible to perfectly meet them all. The problem then resolves itself into a compromise but, rather than an arbitrary one, a highly scientific one requiring an expert with the keenest analytic judgment.

4. *Narrowing the Field.* — With the general scope of the particular problem in mind, the engineer begins to narrow the field for investigation. Obviously he is anxious to make his selection of the site as economically as possible and, therefore, uses every means at his disposal to reduce to a minimum the territory which he must cover in his field investigations. Under the heading "Relation of Specific Fundamental Requirements" many of the ways by which the field is narrowed have already been discussed. It would not be possible to anticipate all of the factors which tend to restrict the investigations to certain areas — each problem

develops its own peculiarities. The engineer now has only one set of tools with which to work — the general plant require-ments and their relative value in respect to costs. Usually he first selects the one or two most important requirements. These must first be met as fully as possible. They may be labor and water, power and waste disposal, raw materials and markets or any other individual requirement or combination of require-ments. To take a case previously mentioned, that of good cheap labor and cold water, the requirements are conflicting and a compromise must be made. As far as these two requirements are concerned the best location will probably be somewhere between the warmer climate territory where the lower wage rates prevail and the colder climates where the water of a lower tem-perature is to be found. Again a consideration of markets and raw materials or some other requirement will probably narrow the field in the other direction, then the engineer has a restricted area upon which he can concentrate more intensively and an area which is entirely practicable to cover in a reasonably short time with his field investigations.

5. *Specific Geographic Locations.* — At this stage the engineer refers to an up-to-date atlas, and from the maps visualizes the general territories which are to be considered. Depending on the relative value of the various requirements he may select a number of possible locations. If the requirements are such that appar-ently the plant should be located near the centers of population he slects the more prominent cities in the territory; if the plant is to be located some distance from a town or city he must con-sider such things as a satisfactory source of labor supply, water requirements and desirability of being near a large stream, amount of land and type of topography desired, transportation facilities, etc. To obtain a better idea of the general area being considered reference should be made to the U. S. Geological or other maps which show the topography as well as other details of the area. These maps are exceedingly valuable and should always be available for the plant location engineer's use. When several tenative selections have been made the next step is to gather from office records, chamber of commerce statistics, public libraries, Government publications, etc., all available data rela-tive to these locations. It will be noted that up to this point no field investigations have been made.

*6. Preliminary Field Studies — Obtaining Data.* — The next step is the field investigation of these tentative locations, obtaining all the data that would have any bearing on the cost of constructing and operating the proposed plant at the various sites.

Strange as it may seem, the plant location engineer is often greatly handicapped in obtaining the necessary data. In the first place his mission is a strictly confidential one. To protect the interests of his company it must not be known that a new plant is contemplated for any locality. If his plans become prematurely known, all possible sites may be immediately purchased and held for fabulous figures. This, in itself, has often kept a deserving locality from having a fine new industry in its midst. Commercial organizations are now located in almost every town of any appreciable size and the business of these organizations is to secure new industries for their communities. Very often the aggressiveness and zeal of the men directing these organizations defeat their own purpose. They are so anxious to know what concern is coming to town, how large the plant will be, how many will be employed and a thousand other details that cannot be given out at this time, that they embarrass the engineer and even discourage his attempts to obtain the very information which may lead to the ultimate benefit of their community. Very often he must use every means to conceal his identity and certainly his business. Occasionally in communities the engineer will find a friend who can help him obtain the data and who can be depended upon to keep any confidences. When this is the case the obtaining of data is relatively easy.

The specific data to be obtained cannot be completely listed to fit every plant location problem. Each problem will require special data peculiar to it and this can only be determined when the specific problem is known. The general data, more or less common to all plants, is listed as follows with possible sources from which these data may be obtained shown in parentheses.

1. *Location*
    *A.* Section of the country, state, province, county, etc.
    *B.* Relation to main river, stream, lake, ocean, etc.
    *C.* Distance and direction from surrounding towns and cities.
    *D.* Area covered by city or town.
    *E.* Altitude above sea level.
       (Maps, City Engineer's or local officials)

2. *Population*
    *A*. Present, in city proper.
    *B*. Previous annual or census records — showing rate of growth.
    *C*. Within the trading or public utility zone — reflecting available labor.
    *D*. Percentage of white, colored and various nationalities.
    *E*. Percentage of male and female — white, colored and foreign.
    *F*. Percentage of industrial workers.
    *G*. Percentage of English reading.
    *H*. Number of families.
       (Census records, Chamber of Commerce, local officials)

3. *Transportation Facilities*
    *A. Railroads*
       (*a*) Names of railroads and general territories served.
       (*b*) Number of passenger and freight trains in and out per day.
       (*c*) Belt lines.
       (*d*) Switching charges.
       (*e*) Freight rates and service in- and out-bound.
    *B. Trolleys and Interurban Railways*
       (*a*) Name of corporations owning and operating systems.
       (*b*) Type and kind of system and service.
       (*c*) Sections of city and adjacent towns served.
       (*d*) Fares to different sections of city and nearby towns.
       (*e*) Time consumed in transit to various sections and towns.
    *C. Navigable Waters and Streams*
       (*a*) Names of each.
       (*b*) Draft of boats accommodated.
       (*c*) Names of companies and kind of service rendered.
       (*d*) Territories served.
       (*e*) Rates.
       (*f*) Time in transit to various main points.
    *D. Highways and Bus Systems*
       (*a*) Kind of highways.
       (*b*) Surrounding towns and cities served.
       (*c*) Type and kind of bus service.
       (*d*) Rates to surrounding main towns and cities.
          (Maps, Chamber of Commerce records, transportation officials, tariffs, local officials)

4. *Industries and Products*
    *A*. List of principal industries, with products and number employed, divided between male and female.
    *B*. Total number of manufacturing plants.
    *C*. Total number of manufactured products.
    *D*. Annual output of plants in commodity units or value of finished product.
    *E*. Competing plants.
       (*a*) Fullest possible data as to output, markets, employes, wage rates, etc.
          (Chamber of Commerce records, principal plant officials, personal investigation and observation)

5. *Labor*

    *A.* Prevailing industrial wage rates — male and female.

        (*a*) Rates of industrial workers comparable to those in proposed plant.

    *B.* Wage rates in building trades.

    *C.* Prevailing rates of stenographers, clerks and salaried employes.

    *D.* Employment situation — availability of workers.

    *E.* Records of strikes, discontent, radical agitations, etc.

    *F.* Legal or customary hours per week for industrial workers.

        (Chamber of Commerce, leading industries, employment offices and local officials)

6. *Power*

    *A.* Name of company.

    *B.* Rate schedules — domestic and industrial (light and power).

    *C.* Quantity of power available, voltages.

    *D.* Coal

        (*a*) Sources, sizes, kinds, price, freight rates, analysis.

        (Power companies, coal companies, Chamber of Commerce, railroads)

7. *Water*

    *A.* List of sources, depth and capacity of wells, flow of creeks or rivers.

    *B.* Quantities available — minimum *daily* flows.

    *C.* Analyses — chemical and bacteriological.

    *D.* Rates — domestic and industrial.

    *E.* Temperatures — maximum and minimum.

        (Maps, government records, water companies, Chamber of Commerce, local officials, industries)

8. *Waste Disposal*

    *A.* Restrictions — local and federal laws.

    *B.* Location of city or other important intakes from streams, lakes, etc.

    *C.* Proximity and size of towns on streams.

    *D.* Dependency of towns — below for water supply; above for waste disposal.

    *E.* History of local agitation concerning stream pollution.

        (Local officials, Chamber of Commerce, maps, main industries)

9. *Living Conditions*

    *A.* General appearance of town or city.

    *B.* Miles of railways, paved streets, water lines, sewers.

    *C.* Number of hotels (size), banks, schools, churches, parks and recreation facilities.

    *D.* Type of government, general aggressiveness, etc.

    *E.* Housing situation

        (*a*) Type and number of houses available, building activities, etc.

        (*b*) Sale prices, rents.

    *F.* Living costs — food, clothing, pleasures, luxuries, etc.

        (Observation, Chamber of Commerce, local officials, newspaper ads, etc.)

10. *Climatic Conditions*
      *A*. Records of rainfall, temperature, humidity, prevailing winds.
            (Government records and Chamber of Commerce)
11. *Taxes*
      *A*. City, county and state rates on land and buildings and basis of valuation.
      ·*B*. City, county and state and federal rates on corporate profits.
            (Local officials, main industries and Chamber of Commerce)

12. *Maps, etc.*
      *A*. Local maps, postal card and airplane views, etc.
            (Hotels, City Engineer, local officials, Chamber of Commerce)
13. *Sites*
      *A*. Location of sites investigated, shown on maps.
      *B*. Site data
          (*a*) Ownership, price, etc.
          (*b*) Area, shape, topography, general appearance and adaptability.
          (*c*) Facilities — transportation, water, power, waste disposal, etc.

It is evident that a great many details must be kept in mind by the engineer when he is making his preliminary investigations of a location. Obviously he cannot remember all of the points concerning which he must obtain data and it will be found very convenient to make an outline similar to the above in a loose leaf notebook, leaving appropriate blank spaces for writing in the data obtained in the field. This procedure will avoid overlooking any important information and automatically arrange his notes in a logical order for the writing of the preliminary report.

*7. Preliminary Report and Further Narrowing of Field.* — With the field notes arranged in accordance with the foregoing outline, the report may be written with the least effort. This preliminary report will simply be an enlargement and full explanation of the engineer's field notes and in addition should contain a summary, not over two or three pages in length, from which the company's executives and higher officials can obtain the essential points of the report without the necessity of reading all details. However, the details will be there for those who care to have the complete report of any phase of the investigation. This summary should have the investigated locations arranged in tabular form showing a synopsis of the findings of the field investigation. For an idea of the form of this synopsis see Table II, page 527.

The preliminary report with the summary will include the engineer's recommendations as to the outstanding locations. If the investigation has covered 30 or 40 locations, there may be 10

or 15 of these which will apparently be better suited to the proposed plant than the others. Some, perhaps many, of the sites investigated will be outstandingly unsuitable in some major and vital respects. Those locations can evidently be eliminated from further consideration and the field narrowed down to that extent. In fact, all locations may be eliminated from the first investigation and another field study be necessary. Not infrequently a proposed plant may be contemplated for some entirely new process going through a period of development while the first field investigation is in progress. Later developments in the process may materially alter the first general plant requirements and entirely change the location of the general area which first appears most favorable. Of course, when this occurs, it is necessary to start again with the revised requirements and similarly develop up to this point a new plan for investigation.

Regardless of the number of times this procedure must be followed it is assumed that the preliminary report has been written and contains at least a few possible locations, others having been culled out after the preliminary field study. We are now at the stage where it will be assumed that certain locations ranging from fair to good or excellent remain, and the engineer is now concerned with a more intensive study of these particular locations.

*8. Cost Study — Specific Locations.* — Of all the steps of site selection this one is by far the most important for the estimates of costs must be as nearly perfect as it is humanly possible to make them, otherwise the conclusions will be erroneous and all of the previous work valueless. Cost studies of this type must of necessity be based on many assumptions but these must represent the keenest judgment and most deliberate thought of all concerned and dare not be mere hasty guesses. The future welfare of the proposed plant, if not of the entire company, is now at stake and errors must not be made.

The cost study consists of estimates of the cost of constructing and operating the plant at each of the selected locations. Every item that enters into the construction of the plant and every expense that can be foreseen to enter into the cost of operation is included in this study. An idea of some of the main items to be considered under each of these headings is shown in Table I, accompanying the paragraph on "Fundamentals of Plant Location." When this is completed the unit production cost is

determined for each location.   This unit cost equals the oper-
ating cost divided by quantity of finished product.

The arrival at the unit cost of production is outlined above in
a few words but the actual process is long and painstaking and
requires almost endless detailed discussions and revisions before
the end is reached and approved by all who have been called in to
assist in this cost analysis.   Of course when the unit cost
estimates are finished the matter of selection is almost automatic-
ally completed.   As the location with the lowest unit cost wins,
the estimates must be as nearly correct as possible.

*9. Selection of a Few Outstanding Sites.* — When a large
plant is contemplated involving an initial cost of millions of
dollars, the decision should never be hastily made.   The unit
cost for, say the three best locations, may only vary by fractions
of a cent.   It will be realized that all these estimates, regardless
of the care and precision exercised in making them, are based on
many assumptions.   The company wants to be even more sure
that these assumptions, made as a result of the preliminary in-
vestigations, are correct and they, therefore, plan to option two
or three of the outstanding sites.

*10. Real Estate and Property Options.* — The sites at two or
three locations may be optioned for a period of say 90 days.
Usually at this stage the news of the proposed plant can no
longer be held secret but even here great care must be observed
by all concerned that no individual locality is given definite
promises and it must be made particularly clear that the matter
is not concluded, but only receiving further investigation.

*11. Detailed Studies.* — As soon as the properties are optioned,
engineers are sent on the ground to make detailed surveys, maps
are drawn, layouts are made and tentative preliminary designs
of buildings and structures are prepared.   The period of the
option is simply a proving period to see that the final and more
detailed investigations bear out the findings as covered in the
preliminary report.   During this period every phase affecting
the cost of construction and operation of the plant is studied.
Some of these studies will include: soil bearing tests and exam-
inations, drilling test pits, wells, borings, etc., measurements of
water supplies, checking water qualities and temperatures, labor
surveys, power studies, waste disposal plants, recheck of freight
rates, housing situation, taxes, etc.   After these studies are
completed, the entire cost study is reviewed and revised in

accordance with the lastest developments of the field investigations. Some of the original assumptions will need to be altered but eventually the final estimates of the unit cost of production at these two or three locations are completed.

*12. Selection of Site.* — Now from the cost study the actual selection of the site is made. Of course, it is chosen on one basis — that of costs. Regardless of any other consideration the location where the finished product can be produced and marketed the cheapest is the one and only place for the particular plant. *The site is selected*, other options are forfeited or taken up and the properties retained for the company's future use or held until a resale can be made to advantage. Funds are appropriated and construction starts at the chosen site.

**A Concrete Example.** — Obviously in illustrating the preceding method by a concrete example, everything pertaining to manufacturing processes, locations and costs must be fictitious. No maps of any country have been used as it is desirable to avoid favorable or unfavorable comments upon any locality. The one exception to this is the maps of the United States on which certain wage statistics are shown. This information, however, is public and available to anyone desiring to obtain it. The data itself is not intended to be of value as it is from 3 to 5 years old. The purpose of these charts is to show how the engineer may record and use statistics to give him a broad view of the trend of any phase of his problem. This example is purely fictitious, as well as the cost data; no actual process could be singled out and used as an illustration as some details of processes may be secret and their costs, even though fictitious, might be interpreted as intended to apply to some actual plant. The purpose of this example is only to further clarify the procedure of the engineer in selecting the location for a proposed plant.

*General Plant Requirements.* — It is assumed that the engineer has spent several days with executives of his company who have explained that the demand for some one of their products has increased beyond their manufacturing capacity and that every indication points toward an increasingly greater and greater demand. One section of the country is, as yet, scarcely familiar with the many uses of the product and it is primarily this territory which is proposed to be served.

Then the general requirements are as follows:

*A. The Plant.* — The name of the product to be manufactured. One unit of the plant will be built first, having a capacity of 30,000 tons per year (56,250,000 gallons). Eight units are eventually contemplated.

*B. Locations.* — The market for the finished product for at least six units will be entirely within a certain radius of Bank City. Probably by the time 8 units are completed, this market will absorb the entire output. If such is not the case the additional output, over six units, will be shipped to the plant at Boontown. The amounts of raw materials for one unit, together with the sources, are:

| Raw Material | Quantity per Unit per Year | Possible Sources |
|---|---|---|
| Acid...............................20,000 tons. | | Blue Point Acid City Sulfuric Aceticville |
| Sodium hydroxide................. 2,000 tons | | Base City Alkali Sodaville |
| Solvent........................ 500 tons | | Faraway City |

An industrial village is to be avoided if possible.

*C. Land.* — For the ultimate expansion, 50 acres of level land are required. Buildings of first unit will cover about two acres, other units must be separated.

*D. Labor.* — Approximately 1200 industrial workers for the first unit, 1000 for each of next three units and about 900 for each of the four remaining units, all female, except a few janitors, laborers and the supervisory force will be required. A good grade of worker is needed — intelligent but not necessarily skilled. Ultimate number of employes — 7800.

*E. Power.* — Electric power — one unit — maximum monthly consumption 1,000,000 k.w.h. with a peak load of 3000 kw.

Coal — 8000 ton good grade steam coal required for one unit per year.

*F. Water.* — For one unit 1000 g.p.m. of soft cold water free from iron. For eight units 8000 g.p.m. of soft cold water free from iron.

*G. Waste Disposal.* — For one unit 600 g.p.m. and for 8 units 4800 g.p.m. Nature of waste is not injurious to stream life but

may impair water for drinking purposes unless at least 20 for 1 dilution can be obtained.

*Relation of Specific to Fundamental Requirements.* — After receiving the specific plant requirements the engineer studies their relations to the fundamental requirements — costs. In the first place, 50 acres of level land is required fairly near a city. Then it is noted that about 7800 female workers are needed and from previous cost records it is found that labor costs are apt to form nearly half the unit cost of the finished product. Thinking always of costs, the engineer at once realizes the necessity of good labor at low rates. Furthermore, he anticipates the possibility of a location near a city where the industrial life is at present unbalanced, i.e., where men are in great demand and few of the industries use women workers. A city which enjoys a balanced industrial life is less apt to experience unrest and discontent because diversity of industries and employment of male and female workers tends to eliminate great peaks or depressions in a locality's prosperity. Also it is noted that considerable power is required — large savings may be effected if the plant makes its own power; steam coal prices and qualities are important. The requirement of cold water conflicts with cheap labor and some compromise may be necessary. It is found that one half of the water required must not exceed 60° F. at any time and if the water exceeds this temperature a refrigeration plant must be installed which will add 50¢ per ton to the cost of the finished product for each ten degrees of temperature over 60° F.

Comparing the effect of the cost of cold water with that of labor it is seen that an average increase of 50¢ per week in the wage rate (without an increase of production) would increase operating costs $31,200 (50¢ × 52 weeks × 1200 workers) per year and raise the unit cost of production $1.04 ($31,200/30,000 T.) per ton. Therefore, any compromise between cold water and low wage rates will probably lean toward the favoring of the latter even though refrigeration is necessary. From the general requirement in regard to waste disposal, it is evident that discharge into a large body of water is desirable.

*General Scope of Investigation.* — Taking the foregoing into consideration, the scope of the investigation must be planned with a consideration of markets and raw material sources.

First consider the markets for the finished product. On a map of the country (see Fig. 167) Bank City is located. Three-
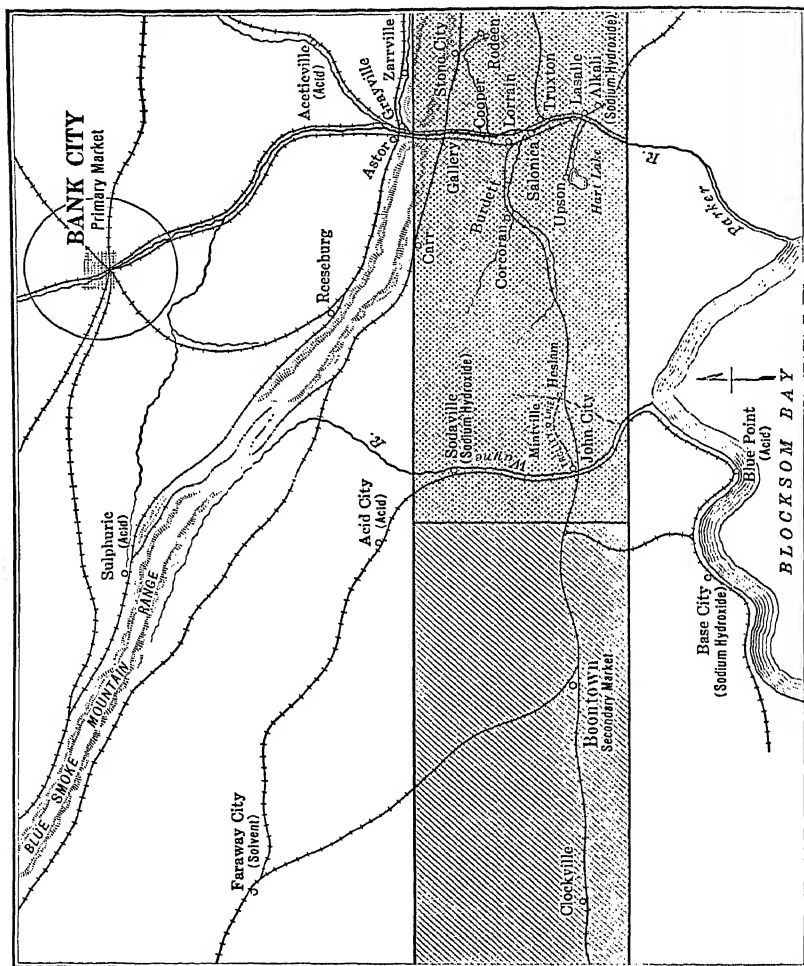
FIG. 167.  Map Showing Markets.

fourths of the finished product will be shipped to this point and the balance may be consumed here or shipped to the Boontown Plant. A circle with a given radius is drawn around Bank City to represent the main market. From the map it will be noted that a mountain range extends from northwest to southeast. Boontown is underscored to bring out the relative location of a secondary market. Railroad lines extend along the foot of this range on both sides. One railroad cuts across this range but grades are heavy and the route is very circuitous.

*Narrowing the Field.* — Since labor rates play such a vital part in the cost of the unfinished product, the engineer studies all sources of industrial rate data at his disposal. The U. S. Department of Labor publishes statistics showing the average earnings per hour in various industries for various sections of the Unites States. Other countries have similar statistics available. Several maps of the United States are appended hereto showing the published wage statistics for a few trades — see Figs. 168, 169, 170. Similar data can be obtained for various sections and for various industries. The engineer may find statistics exactly fitting the industry under consideration but if not, these statistics for similar industries will be invaluable as a general guide to the trend of industrial rates. From even these three plates it is very noticeable that the lower rates prevail in the warmer climates and the underlying reason is lower living costs as outlined in the foregoing text.

In this particular problem it is now assumed that the engineer has studied the labor statistics for the country under consideration. He finds that the general trend of lower wage rates in industries similar to the proposed plant extend across the country in a belt as shown shaded on the map (Fig. 1). This in a general way limits the area for an investigation in a northerly and southerly direction. Still lower rates may be found below this belt but generally speaking the climate is much warmer and less desirable. The engineer's knowledge of this section, borne out by statistics available, shows that though industrial rates in this section may be somewhat lower the type of worker is less desirable and the quality and quantity of production is adversely affected. Therefore, for the time being he confines his thought to the belt described above.

Next, raw materials and markets are considered.
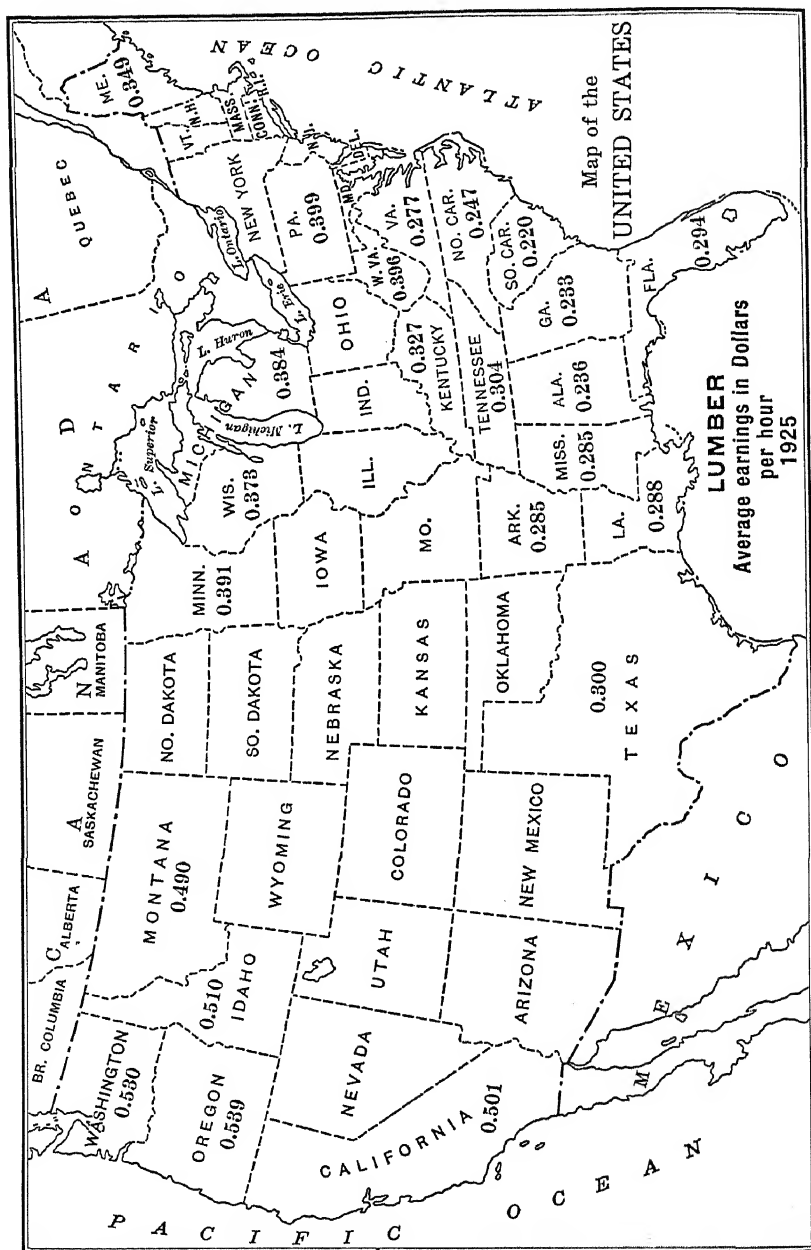
Fig. 168.   Average Wages in Dollars Per Hour in the Lumber Industry.
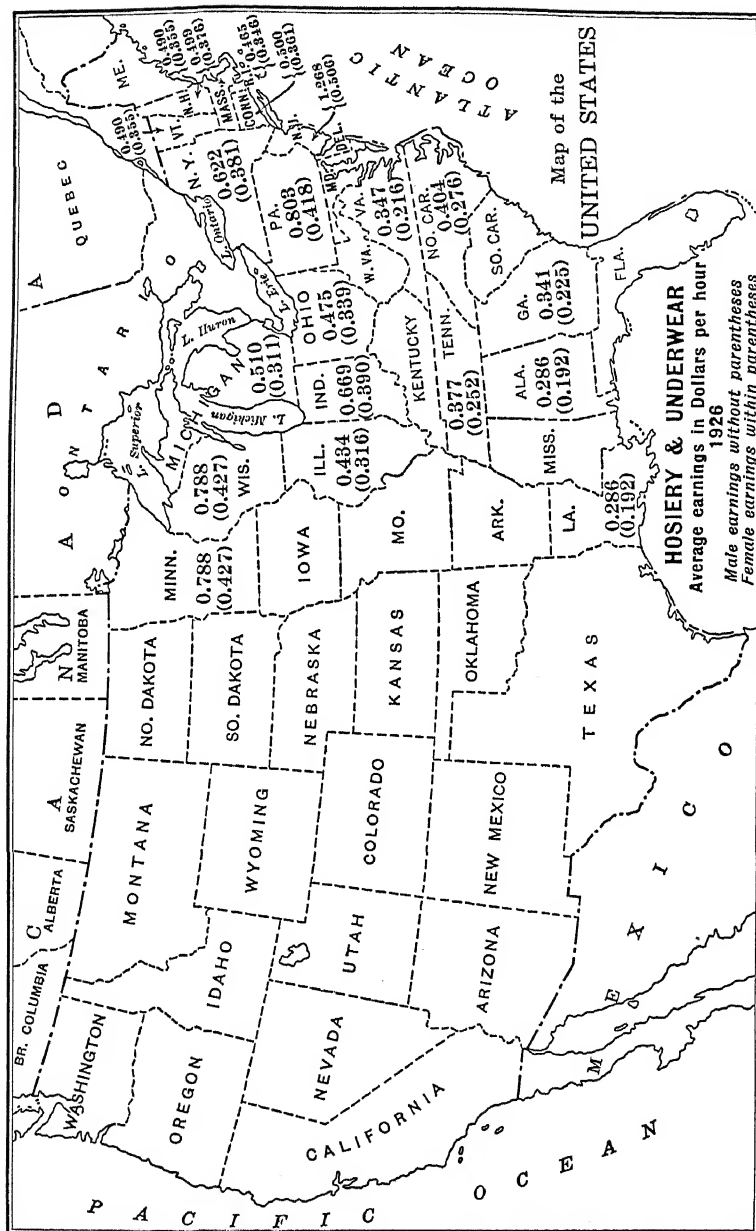
FIG. 169. Average Wages in Dollars Per Hour in the Hosiery and Underwear Industry.
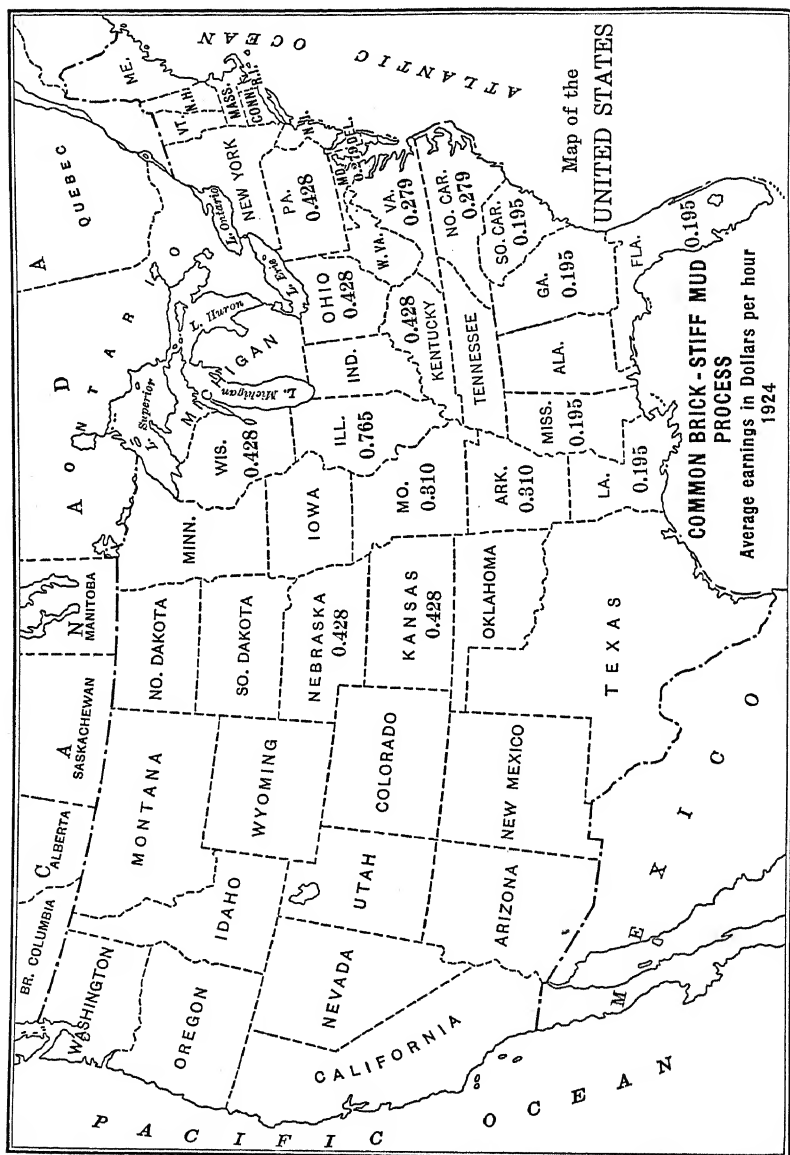
FIG. 170. Average Wages in Dollars Per Hour in the Brick Industry.

The sources of raw materials are marked on the map (Fig. 167). The main bulk of the raw materials is the acid and this must receive the greatest consideration. The transportation systems now come into consideration, for the engineer desires the shortest possible haul for raw materials as well as for finished product. As a rule, long "back hauling" of materials is to be avoided. For instance, consider a location at Clockville. This place is not centrally located with respect to raw materials or markets. Wherever the raw materials might be obtained they would have to be hauled long distances (high freight costs) to Clockville and then the finished product "back hauled" over a part of the same long route to the market. Therefore, the engineer desires to first consider a general location somewhat centrally located with respect to markets and raw materials. By the trend of lower labor rates the field has been narrowed in a northerly and southerly direction and now from consideration of raw materials and markets it is possible to narrow it in an easterly and westerly direction, approximately within the limits cross-hatched on the map.

*Specific Geographic Locations.* — The engineer now obtains a larger map (see Fig. 171) of this particular area and since his officials, on account of predetermined costs, desire to have the plant fairly near a city where labor supply is ample and the housing problem is not encountered, he selects the important cities of this area. These cities are shown on the larger map of the area — Fig. 171.

*Preliminary Field Study.* — The selected locations are now investigated in the field and the data obtained as outlined in the foregoing text.

*Preliminary Report — Further Narrowing of Field.* — Space prohibits giving a detailed report of the findings at each location. A full report is written and the summarized synopsis of the twenty locations investigated is given in Table II. From this summary it is evident that six of the locations (Nos. 2, 9, 11, 14, 15 and 19) are outstanding and that anyone of these locations would be preferred to anyone of the remaining fourteen. The field then becomes narrowed to the six cities of LaSalle, Cooper, Burdett, Salonica, John City and Grayville.

*Cost Study.* — The cost of constructing and operating the plant at these six locations is most carefully estimated, taking all factors into consideration. The preliminary results of this analysis are
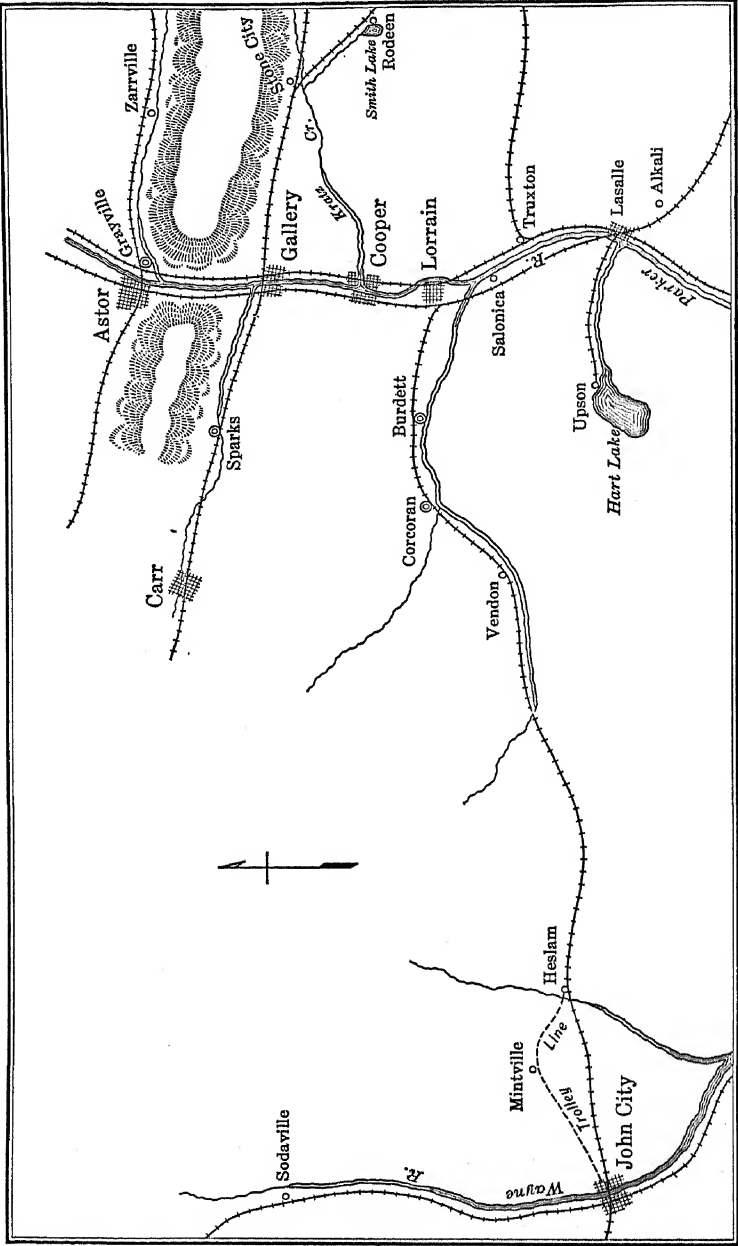
Fig. 171.   Map Showing Location of Cities.

TABLE II. — SUMMARIZED SYNOPSIS OF SITE INVESTIGATIONS

| Location | Population | Transportation Facilities | | Labor | | | Power Costs | Water | | Waste Disposal | Taxes (100% Basis of Valuation) | Sites | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Railroads | Bus and Trolley Service | Quality | Quantity | Rates | | Quality | Quantity | | | | |
| 1. Upson | 5,200 8.7% colored | Only one branch railroad. Service seems very poor | No trolleys. Fair bus system | Appears to be good | Very doubtful unless a large territory could be drawn on | $9–12 week | Probably fairly low | Very good | Ample at all time | No restrictions | $1.10 | One good site. Very cheap. $25 per acre | Town is quite progressive. Very anxious for new industries. Growth has been rather slow |
| 2. LaSalle | 43,600 10% colored. 2% foreign | Three railroads. Two trunk lines, one branch line | Trolleys good, 10¢ fare. Busses good but few of them | Good. No strikes or labor troubles in past 30 years | Ample | $11.00 week | Fairly low. Lower tariffs may be issued in one year | Contains some iron. Otherwise good. Samples being tested. Max. temp. 58° | Fair. Probably O.K. but needs further investigation | No restrictions for five years | $1.50 | One good site. $200/A. One fair site $50/A. | City appears progressive. Evidence of civic pride. Active Chamber of Commerce. Home well kept up |
| 3. Corcoran | 28,000 11% colored. No foreign | Two railroads. One trunk line and one branch line | Fair trolley service at one time. Busses are now replacing trolleys | Fair | Ample untrained | $10–12 week | Extremely high. Coal prices also very high | Good | Limited. May have to depend on wells to large extent | Beginning to require treatment of waste | $1.80 | One site near RR and river very good. $200–$250/A. | Long standing fight between political factions in regard to power companies entering town. No evidence of early settlement |
| 4. Vendon | 8,742 65% colored | One trunk line. Service good | Small trolley system. Poorly patronized | Very good | Very few white female workers | Low for colored. Rather high for white workers | Moderate | Very good. May be muddy in Spring | Fair supply. Probably O.K. | No restrictions | $0.87 | One fair site. Four miles from town | City very anxious for new industries. Quite aggressive |

TABLE II. — *Continued*

| Location | Population | Transportation Facilities | | Labor | | | Power Costs | Water | | Waste Disposal | Taxes (100% Basis of Valuation) | Sites | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Railroads | Bus and Trolley Service | Quality | Quantity | Rates | | Quality | Quantity | | | | |
| Darr | 50,000 40% colored | One trunk line | No trolley. Fair bus service | Fair. Not many industries | Supply would probably be ample | $10–15 week | Reasonable. Coal rates quite low | Very hard. Otherwise very good | Supply consists of mountain streams. City uses practically all of available supply | No restrictions at present | $2.00 | Two available but not especially level. Price from $200 to $500 per acre | Not an industrial town. Very largely a resort town. Many inns and hotels of good appearance but residential section quite shabby |
| Lorrain | 33,300 2% colored. No foreign | Two trunk lines. Very good service | Excellent bus and trolley system. Belt line around city. Trolley fare $0.05 | Very good | Ample supply | $9–11 week | Very low | Chemical analysis appears excellent | Good quantity. Several large springs | Restricted on account of cities on river below Lorrain | $0.60 | No available sites near town. All available level land in use | A good industrial town but appears to be quite overcrowded |
| Vallery | 97,264 12% colored. 8% foreign | Three trunk lines. 75 trains per day | Trolleys good. $.07½ fare. Transfer system. 3 large bus lines | Excellent. Very low labor turnover in industries | Very large | $8–14 week | New hydroelectric plant being built. Expect very low rates | Extremely poor. Many industries have difficulties with water | Ample but badly contaminated with mine wastes | No restrictions | $4.85 | Two good sites but prices range from $3000–$4000 per acre | City fairly aggressive. Two bitterly opposed political factions |
| Yuxon | 7,774 No colored or foreign | Two RR's, one trunk line. Good service | No trolleys. Good bus service. Low rates | Good | Fair. Should be investigated | One industry pays female workers $7/week. Other industries are very small | No definite data obtainable | Must be filtered and treated | Sufficient | No restrictions for 5–10 years at least | $1.05 | One very good site. Cheap. Probably less than $40/acre | Town is most unprogressive. Ten years ago population was over 15,000. Each year has shown a decrease in population |

TABLE II. — Continued

| Location | Population | Transportation Facilities | | Labor | | | Power Costs | Water | | Waste Disposal | Taxes (100% Basis of Valuation) | Sites | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Railroads | Bus and Trolley Service | Quality | Quantity | Rates | | Quality | Quantity | | | | |
| 9. Cooper | 31,000 12% colored. 1% foreign | Two trunk line RR's. Inter RR transfer | Trolleys fair, $.07 fare. 20 busses per day to near-by towns | Very good | Large supply | $9/week | Very low. Coal rates very low | O.K. See analyses | Unquestionable supply. Many large wells. Max. temp. 62° | Some industries treat wastes | $0.98 | Three good sites. One site priced at $50/acre, one RR at each site | Fine houses. Very business-like appearance |
| 10. Sparks | 18,020 2% colored. No foreign | 1 trunk line, RR service fair | Trolleys may be abandoned in one year. Trolley Co. operates busses | Good | Supply has seldom kept pace with demands | $20–30/week. Spoken of as the city of million-aire wages | Very low | Good | Questionable. Industries do not require large water supplies | Very apt to be restricted | $1.35 | Only one available site which is at all suitable | People spend money freely, Labor rates are abnormally high for this section because demand has always exceeded supply |
| 11. Burdett | 15,800 No colored practically | 1 trunk line RR. Good service | No trolleys. Busses adequately serve town | Good | Supply should be checked | Average $10–13/week | Low electricity made with water power. Coal rates medium | Very good. Max temp. 70° | Almost unlimited | Treatment probably required | $1.00 Rate may increase | Two good sites. Prices rather high about $250/A. | Town has good general appearance except S.E. section |
| 12. Astor | 168,490 23% colored | 2 trunk line RR's. 140 trains per day | Trolley and interurban system very good. Bus and trolley rates low | Fair | Ample | $12–16/week | Not very low. Coal prices medium | Doubtful. River is highly contaminated with wastes from plants above city | Very large | Down stream towns are uniting to force elaborate treatment of plant wastes | $1.67 | One excellent site, $500/acre. Two fair sites also $500 per acre | Many excellent homes. Apparently a city of considerable wealth. Many banks with large resources. Attractive business section |

TABLE II. — *Continued*

| Location | Population | Transportation Facilities | | Labor | | | | Water | | | Taxes (100% Basis of Valuation) | Sites | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Railroads | Bus and Trolley Service | Quality | Quantity | Rates | Power Costs | Quality | Quantity | Waste Disposal | | | |
| 13. Stone City | 4,397 No colored. No foreign | 1 trunk line. One branch line. Service fair | No trolleys. One bus line. Service every two hours | Excellent. Thrifty Scotch-Irish, hard workers | Claimed to be ample. Must draw on surrounding communities | $9–10/week | Coal rates are low. Power costs probably low also | Underground supply good. Surface supply has some mineral impurities | Believed to be adequate. Test wells should be driven | Treatment may be required in a few years | $0.84 | Two good sites. Either may be given to a good industry | Housing problem must be encountered. Town seems positively opposed to building any houses for a proposed industry |
| 14. Salonica | 14,490 8% colored | One trunk line. Excellent service | Trolley and bus system very extensive | Some industries have large turnover but many do not experience this | Apparently ample | $9–13/week | Fairly low. Coal also reasonable | Doubtful. Requires further examination. Max. temp. 72° | Very good supply from two sources | Treatment possibly required | $0.75 | Four good sites. Any one satisfactory. Rates factory fairly high | Aggressive and progressive small city. Has had steady growth |
| 15. John City | 27,950 No colored | Two trunk lines. 45 trains daily Boat transportation also | Trolleys abandoned. Excellent bus service | Many industries report excellent quality | Very few women employees. Women go elsewhere for work | About $10/week | Low coal prices via RR medium. Waiting for coal price via boat | Excellent. Max. temp. of Spring 55° | Believed to be ample. One very large spring 8000 g.p.m. | No restrictions for at least ten years | $0.44 | Two sites. excellent site. Price $600/acre | Unbalanced industrial community. Men in great demand. Few women employed. Town seems progressive and up-to-date |
| 16. Zarrville | 12,303 38% foreign 10% colored | One trunk line RR. Service only fair | Trolley system seems very dilapidated. Two bus lines with irregular service | Highly unionized | Apparently ample | $12–14/week | Fairly high. Coal prices moderate | Contaminated with mine wastes | No underground supplies. Max. temp. 82 F. | Unrestricted at present | $1.19 | One good site. Price about $50 per acre | Town has had eight major strikes in past decade. Trolley Co. workers have been out for nine months |

TABLE II. — *Continued*

| Location | Population | Transportation Facilities | | Labor | | | Power Costs | Water | | Waste Disposal | Taxes (100% Basis of Valuation) | Sites | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Railroads | Bus and Trolley Service | Quality | Quantity | Rates | | Quality | Quantity | | | | |
| 17. Mintville | 11,000 4% colored. No foreign | No railroads. Interurban handles freight from Heslam | Good interurban system. Rates quite high | Fair | Doubtful. Not really an industrial town. Mostly retired farmers | No definite rates obtainable | No industrial rates established | Very good. See analysis | Supply may be limited. Under ground water supply good | No precedent | $0.89 | Three very fine sites but two are from 3-5 miles from town | Very attractive homes. Town is quiet and everyone is apparently taking life easy |
| 18. Heslam | 7,000 5% colored. 5% foreign | One trunk line RR. Service good | No trolleys. One fine interurban to Mintville. No busses | Fair. Some strong unions. Last strike 8 years ago | With Mintville and two or three nearby towns there may be sufficient | One of leading citizens states $10-12 rate would attract unlimited supply | Probably have to make own power. Coal is $4.50 ton from Chaymont fields | Samples forwarded to chemists | Good | No restrictions now. State may require treatment in future | $1.41 | Four sites, all very good. Prices from $25-$50 per acre | Not very aggressive. Many people have made money here and retired in Mintville |
| 19. Grayville | 15,432 | Two trunk lines. Very good service | Good trolley and bus systems | Medium | Probably sufficient | Rates seem to vary from $8-$16 per week | Relatively high. Coal prices medium | Very hard. Otherwise seems O.K. Max. temp. 65° | Good | May have to treat wastes | $1.27 | Six good sites. One very good which city will donate | A thriving community. Has several good industries. Industrial workers' homes very neat |
| 20. Rodeen | 5,000 | One branch line | | | | | | | | | | | A college town. Population includes 4,000 students. No further investigation made |

shown in Table III. It will be noted from this tabulation just what particular costs affect adversely or favorably each location.

*Selection of a Few Outstanding Sites.* — The analysis in Table III has developed the fact that it is estimated if the plant is constructed and operated at Cooper or John City the lowest cost of the finished product in dollars per pound will be obtained. The estimates for these two cities are very close, while the next location (LaSalle) is only a fair third choice. Of course, several sites were investigated at each location and the advantages and disadvantages considered in the details of the cost analysis but not shown in Table III.

Now some of the assumptions may be slightly in error at any of these six locations but with a full knowledge of the care exercised in preparing this cost data, the engineer feels assured that only gross errors in the assumptions would place LaSalle, Burdett, Salonica and Grayville in close competition with Cooper or John City.

In Table III under "Operating Cost" it is now more apparent than ever that labor costs are vital in their effect on total and unit costs in this particular example. Wage rates enter into many of the items of "Operating Cost" but it will be seen that the one item "Labor" is about five times as great as even the next largest single item. This fact makes it at once evident that even slight errors in the wage rate data obtained may entirely change the standing of any one of these six locations in their final position. It is, therefore, decided to make a more detailed and final analysis of wage rates at all of the six locations, and revise every cost item which is affected by wage rates. It is assumed that this study is completed, wage rates at LaSalle, Cooper, John City and Grayville required revision, while the preliminary data at Burdett and Salonica was found to be correct. This revision of the cost data still shows Cooper and John City as the preferred locations but with John City now making the stronger bid for first place. The relative positions of the four other locations remain unchanged. Therefore, these two latter locations must undergo further detailed studies revealing any necessary corrections to the assumptions and assuring the engineer that the very best selection is ultimately made.

*Property Options.* — The most favorable site at Cooper and John City is now taken under option at a definite price for a period of 90 days. All necessary rights of way, permits, priv-

TABLE III. — PRELIMINARY COST ANALYSIS OF SIX OUTSTANDING LOCATIONS (ONE UNIT)

| Items | LaSalle | Cooper | Burdett | Salonica | John City | Grayville |
|---|---|---|---|---|---|---|
| Investment Cost | | | | | | |
| Real estate............... | $ 12,000 | $ 3,750 | $ 20,000 | $ 18,000 | $ 60,000 | — |
| Rights of way, permits, etc..... | 1,500 | 300 | 2,800 | 2,000 | 4,700 | $ 800 |
| Grading site.............. | 4,840 | 2,420 | 3,980 | 4,440 | 6,800 | 1,600 |
| Plant buildings........... | 1,362,400 | 1,104,200 | 1,357,110 | 1,407,200 | 1,037,000 | 1,040,440 |
| Equipment installed........ | 756,000 | 701,420 | 748,880 | 761,000 | 697,500 | 705,000 |
| Power.................... | 127,600 | 132,110 | 128,000 | 149,770 | 109,070 | 151,100 |
| Transportation............ | 18,390 | 21,500 | 69,910 | 22,630 | 107,410 | 16,600 |
| Water.................... | 92,800 | 85,910 | 56,330 | 78,850 | 119,440 | 71,550 |
| Waste disposal............ | 37,100 | 51,120 | 62,700 | 59,010 | 35,350 | 43,310 |
| Miscellaneous............. | 31,610 | 22,000 | 38,000 | 31,200 | 42,570 | 24,760 |
| Total.................... | $2,444,240 | $2,124,730 | $2,487,710 | $2,534,100 | $2,219,840 | $2,055,160 |

Table III. — *Continued*

| Items | LaSalle | Cooper | Burdett | Salonica | John City | Grayville |
|---|---|---|---|---|---|---|
| Operating Cost (Annual) | | | | | | |
| Freight on raw materials........ | $ 61,250 | $ 48,750 | $ 58,250 | $ 47,000 | $ 45,750 | $ 25,500 |
| Freight on finished product.... | 90,000 | 110,000 | 62,500 | 67,500 | 60,000 | 105,000 |
| Raw materials................. | 97,300 | 97,300 | 97,300 | 97,300 | 82,110 | 97,300 |
| Labor....................... | 690,400 | 561,600 | 717,600 | 708,400 | 624,000 | 748,800 |
| Power (Light, heat, etc.)...... | 81,560 | 43,510 | 77,700 | 75,420 | 66,950 | 104,300 |
| Water....................... | 37,600 | 28,400 | 36,600 | 51,830 | 27,010 | 42,050 |
| Refrigeration................ | | 3,000 | 15,000 | 18,890 | | |
| Storing, packing, etc.......... | 11,090 | 9,010 | 10,300 | 11,090 | 8,000 | 12,310 |
| Supplies..................... | 4,050 | 3,060 | 3,800 | 3,000 | 2,940 | 2,700 |
| Sanitation................... | 7,760 | | 9,550 | 11,600 | 9,600 | 10,060 |
| Repairs, renewals, upkeep..... | 13,600 | 11,000 | 13,600 | 14,100 | 10,400 | 10,400 |
| Supervision and office expenses. | 78,640 | 56,400 | 75,520 | 78,640 | 62,160 | 74,880 |
| Welfare...................... | 30,000 | 35,000 | 40,000 | 25,000 | 30,000 | 10,000 |
| Taxes and insurance.......... | 28,100 | 22,210 | 24,550 | 24,900 | 23,200 | 23,900 |
| Interest on investment........ | 147,000 | 127,500 | 149,220 | 152,040 | 133,200 | 123,300 |
| Depreciation................. | 48,000 | 42,000 | 48,600 | 50,000 | 40,610 | 40,000 |
| Miscellaneous................ | 6,100 | 5,800 | 5,860 | 6,100 | 5,310 | 6,700 |
| Total....................... | $1,432,450 | $1,204,540 | $1,445,960 | $1,442,810 | $1231,240 | $1,437,200 |
| Unit production cost in dollars per ton...... | $47.75 | $40.15 | $48.20 | $48.09 | $41.04 | $47.91 |

ileges, etc., are tentatively entered into in regard to each of these two sites.

*Detailed Studies.* — As soon as options are signed the engineers go upon the ground and survey each location. A property map is made on a scale of 100, 200 or 400 feet to the inch. Topographical maps are prepared on a scale of 40 or 50 feet to the inch. Detail drawings of the plant buildings are prepared and plant layouts are made on the topographical maps. A labor survey is made, test wells are drilled, soil bearing tests and examinations are conducted, water, power and waste disposal investigations are carried out, transportation facilities and freight rates are checked, taxes are tentatively agreed upon and in fact every item entering into costs is examined and compared with the results of the preliminary investigations. The cost figures are then revised as shown in Table IV and by comparing them with Table III the revisions in detail will be noted. The example only shows the preliminary and final cost analysis whereas it may often be necessary to make many of these analyses before the final one is agreed upon. In this case, however, the result now shows John City to have a slight preference over Cooper and though this difference of the unit cost of the finished product in cents per ton is not great, it may be just this difference, in years to come, which will leave the plant on a solid footing to meet the severest competition.

*Selection of Site.* — As may be anticipated, the selection of the site comes automatically with the completion of the cost data. Purchase of land, all permits, etc., are consummated at John City. The land at Cooper may also be bought as the property is cheap and taxes relatively low. Furthermore, the company realizes the value of the Cooper site and does not wish to have a competitor receive all of the benefit of this painstaking and expensive investigation, for it is now publicly known that Cooper must have been a close second choice for the site for the proposed plant. Moreover this land at Cooper may be utilized when demand warrants an additional factory.

TABLE IV. — FINAL COST ANALYSIS OF SIX OUTSTANDING LOCATIONS (ONE UNIT)

| Items | LaSalle | Cooper | Burdett | Salonica | John City | Grayville |
|---|---|---|---|---|---|---|
| Investment Cost | | | | | | |
| Real estate................ | $ 12,000 | $ 3,750 | $ 20,000 | $ 18,000 | $ 60,000 | $ — |
| Rights of ways, permits, etc... | 1,500 | 300 | 2,800 | 2,000 | 4,700 | 800 |
| Grading site.............. | 4,600 | 2,540 | 3,980 | 4,440 | 6,460 | 1,500 |
| Plant buildings........... | 1,328,340 | 1,131,800 | 1,357,110 | 1,407,200 | 1,011,100 | 1,000,000 |
| Equipment installed....... | 737,100 | 718,920 | 748,880 | 761,000 | 680,060 | 701,100 |
| Power.................... | 125,600 | 134,610 | 128,000 | 149,770 | 105,000 | 149,900 |
| Transportation............ | 18,000 | 22,000 | 69,910 | 22,630 | 104,330 | 16,000 |
| Water.................... | 89,600 | 88,450 | 56,330 | 78,850 | 113,400 | 69,220 |
| Waste disposal............ | 36,060 | 54,400 | 62,700 | 59,010 | 32,700 | 41,570 |
| Miscellaneous............. | 30,000 | 23,500 | 38,000 | 31,200 | 38,000 | 22,200 |
| Total................ | $2,382,800 | $2,180,270 | $2,487,710 | $2,534,100 | $2,155,750 | $2,002,290 |

Table IV. — *Continued*

Operating Cost (Annual)

| Items | LaSalle | Cooper | Burdett | Salonica | John City | Grayville |
|---|---|---|---|---|---|---|
| Freight on raw materials | $ 61,250 | $ 48,750 | $ 58,250 | $ 47,000 | $ 45,750 | $ 25,500 |
| Freight on finished product | 90,000 | 110,000 | 62,500 | 67,500 | 60,000 | 105,000 |
| Raw materials | 97,300 | 97,300 | 97,300 | 97,300 | 82,110 | 97,300 |
| Labor | 655,900 | 589,680 | 717,600 | 708,400 | 582,800 | 718,080 |
| Power (Light, heat, etc.) | 78,360 | 45,000 | 77,700 | 75,420 | 62,010 | 100,000 |
| Water | 36,000 | 30,460 | 36,600 | 51,830 | 25,460 | 41,692 |
| Refrigeration | — | 3,200 | 15,000 | 18,890 | — | — |
| Storing, packing, etc. | 10,500 | 9,460 | 10,300 | 11,090 | 7,600 | 12,000 |
| Supplies | 4,050 | 3,060 | 3,800 | 3,000 | 2,940 | 2,700 |
| Sanitation | 7,600 | — | 9,560 | 11,600 | 8,840 | 9,660 |
| Repairs, renewals, upkeep | 12,800 | 11,940 | 13,600 | 14,100 | 9,060 | 9,800 |
| Supervision and office expenses | 80,000 | 62,060 | 75,520 | 78,640 | 56,810 | 76,100 |
| Welfare | 28,900 | 37,500 | 40,000 | 25,000 | 27,750 | 10,000 |
| Taxes, insurance, etc. | 28,100 | 22,210 | 24,550 | 24,900 | 23,200 | 23,900 |
| Interest on investment | 142,980 | 130,800 | 149,220 | 152,040 | 129,360 | 120,120 |
| Depreciation | 47,000 | 43,500 | 48,600 | 50,000 | 40,610 | 40,000 |
| Miscellaneous | 6,000 | 6,000 | 5,860 | 6,100 | 5,000 | 6,700 |
| Total | $1,386,740 | $1,250,920 | $1,445,960 | $1,422,810 | $1,169,300 | $1,398,550 |
| Unit production cost in dollars per ton | $46.22 | $41.70 | $48.20 | $48.09 | $38.98 | $46.62 |

# APPENDIX

TABLE 1. — PROPERTIES OF SATURATED STEAM

Reproduced by Permission from Marks and Davis "Steam Tables and Diagrams"

(Copyright, 1909, by Longmans, Green & Co.)

| Pressure Pounds Absolute | Temperature Degrees Fahrenheit | Specific Volume Cubic Feet per Pound | Heat of the Liquid, B.t.u. | Latent Heat of Evaporation B.t.u. | Total Heat of Steam, B.t.u. | Pressure Pounds Absolute |
|---|---|---|---|---|---|---|
| 1 | 101.83 | 333.0 | 69.8 | 1034.6 | 1104.4 | 1 |
| 2 | 126.15 | 173.5 | 94.0 | 1021.0 | 1115.0 | 2 |
| 3 | 141.52 | 118.5 | 109.4 | 1012.3 | 1121.6 | 3 |
| 4 | 153.01 | 90.5 | 120.9 | 1005.7 | 1126.5 | 4 |
| 5 | 162.28 | 73.33 | 130.1 | 1000.3 | 1130.5 | 5 |
| 6 | 170.06 | 61.89 | 137.9 | 995.8 | 1133.7 | 6 |
| 7 | 176.85 | 53.56 | 144.7 | 991.8 | 1136.5 | 7 |
| 8 | 182.86 | 47.27 | 150.8 | 988.2 | 1139.0 | 8 |
| 9 | 188.27 | 42.36 | 156.2 | 985.0 | 1141.1 | 9 |
| 10 | 193.22 | 38.38 | 161.1 | 982.0 | 1143.1 | 10 |
| 11 | 197.75 | 35.10 | 165.7 | 979.2 | 1144.9 | 11 |
| 12 | 201.96 | 32.36 | 169.9 | 976.6 | 1146.5 | 12 |
| 13 | 205.87 | 30.03 | 173.8 | 974.2 | 1148.0 | 13 |
| 14 | 209.55 | 28.02 | 177.5 | 971.9 | 1149.4 | 14 |
| 15 | 213.0 | 26.27 | 181.0 | 969.7 | 1150.7 | 15 |
| 16 | 216.3 | 24.79 | 184.4 | 967.6 | 1152.0 | 16 |
| 17 | 219.4 | 23.38 | 187.5 | 965.6 | 1153.1 | 17 |
| 18 | 222.4 | 22.16 | 190.5 | 963.7 | 1154.2 | 18 |
| 19 | 225.2 | 21.07 | 193.4 | 961.8 | 1155.2 | 19 |
| 20 | 228.0 | 20.08 | 196.1 | 960.0 | 1156.2 | 20 |
| 22 | 233.1 | 18.37 | 201.3 | 956.7 | 1158.0 | 22 |
| 24 | 237.8 | 16.93 | 206.1 | 953.5 | 1159.6 | 24 |
| 26 | 242.2 | 15.72 | 210.6 | 950.6 | 1161.2 | 26 |
| 28 | 246.4 | 14.67 | 214.8 | 947.8 | 1162.6 | 28 |
| 30 | 250.3 | 13.74 | 218.8 | 945.1 | 1163.9 | 30 |
| 32 | 254.1 | 12.93 | 222.6 | 942.5 | 1165.1 | 32 |
| 34 | 257.6 | 12.22 | 226.2 | 940.1 | 1166.3 | 34 |
| 36 | 261.0 | 11.58 | 229.6 | 937.7 | 1167.3 | 36 |
| 38 | 264.2 | 11.01 | 232.9 | 935.5 | 1168.4 | 38 |
| 40 | 267.3 | 10.49 | 236.1 | 933.3 | 1169.4 | 40 |

Tables 1 and 2 are quoted from "Steam, Its Generation and Use," by The Babcock and Wilcox Company, to which the student is referred for other tables on steam and fuels.

TABLE 1. — *Continued*

| Pressure Pounds Absolute | Temperature Degrees Fahrenheit | Specific Volume Cubic Feet per Pound | Heat of the Liquid, B.t.u. | Latent Heat of Evaporation B.t.u. | Total Heat of Steam, B.t.u. | Pressure Pounds Absolute |
|---|---|---|---|---|---|---|
| 42 | 270.2 | 10.02 | 239.1 | 931.2 | 1170.3 | 42 |
| 44 | 273.1 | 9.59 | 242.0 | 929.2 | 1171.2 | 44 |
| 46 | 275.8 | 9.20 | 244.8 | 927.2 | 1172.0 | 46 |
| 48 | 278.5 | 8.84 | 247.5 | 925.3 | 1172.8 | 48 |
| 50 | 281.0 | 8.51 | 250.1 | 923.5 | 1173.6 | 50 |
| 52 | 283.5 | 8.20 | 252.6 | 921.7 | 1174.3 | 52 |
| 54 | 285.9 | 7.91 | 255.1 | 919.9 | 1175.0 | 54 |
| 56 | 288.2 | 7.65 | 257.5 | 918.2 | 1175.7 | 56 |
| 58 | 290.5 | 7.40 | 259.8 | 916.5 | 1176.4 | 58 |
| 60 | 292.7 | 7.17 | 262.1 | 914.9 | 1177.0 | 60 |
| 62 | 294.9 | 6.95 | 264.3 | 913.3 | 1177.6 | 62 |
| 64 | 297.0 | 6.75 | 266.4 | 911.8 | 1178.2 | 64 |
| 66 | 299.0 | 6.56 | 268.5 | 910.2 | 1178.8 | 66 |
| 68 | 301.0 | 6.38 | 270.6 | 908.7 | 1179.3 | 68 |
| 70 | 302.9 | 6.20 | 272.6 | 907.2 | 1179.8 | 70 |
| 72 | 304.8 | 6.04 | 274.5 | 905.8 | 1180.4 | 72 |
| 74 | 306.7 | 5.89 | 276.5 | 904.4 | 1180.9 | 74 |
| 76 | 308.5 | 5.74 | 278.3 | 903.0 | 1181.4 | 76 |
| 78 | 310.3 | 5.60 | 280.2 | 901.7 | 1181.8 | 78 |
| 80 | 312.0 | 5.47 | 282.0 | 900.3 | 1182.3 | 80 |
| 82 | 313.8 | 5.34 | 283.8 | 899.0 | 1182.8 | 82 |
| 84 | 315.4 | 5.22 | 285.5 | 897.7 | 1183.2 | 84 |
| 86 | 317.1 | 5.10 | 287.2 | 896.4 | 1183.6 | 86 |
| 88 | 318.7 | 5.00 | 288.9 | 895.2 | 1184.0 | 88 |
| 90 | 320.3 | 4.89 | 290.5 | 893.9 | 1184.4 | 90 |
| 92 | 321.8 | 4.79 | 292.1 | 892.7 | 1184.8 | 92 |
| 94 | 323.4 | 4.69 | 293.7 | 891.5 | 1185.2 | 94 |
| 96 | 324.9 | 4.60 | 295.3 | 890.3 | 1185.6 | 96 |
| 98 | 326.4 | 4.51 | 296.8 | 889.2 | 1186.0 | 98 |
| 100 | 327.8 | 4.429 | 298.3 | 888.0 | 1186.3 | 100 |
| 105 | 331.4 | 4.230 | 302.0 | 885.2 | 1187.2 | 105 |
| 110 | 334.8 | 4.047 | 305.5 | 882.5 | 1188.0 | 110 |
| 115 | 338.1 | 3.880 | 309.0 | 879.8 | 1188.8 | 115 |
| 120 | 341.3 | 3.726 | 312.3 | 877.2 | 1189.6 | 120 |
| 125 | 344.4 | 3.583 | 315.5 | 874.7 | 1190.3 | 125 |

TABLE 1. — *Continued*

| Pressure Pounds Absolute | Temperature Degrees Fahrenheit | Specific Volume Cubic Feet per Pound | Heat of the Liquid, B.t.u. | Latent Heat of Evaporation B.t.u. | Total Heat of Steam. B.t.u. | Pressure Pounds Absolute |
|---|---|---|---|---|---|---|
| 130 | 347.4 | 3.452 | 318.6 | 872.3 | 1191.0 | 130 |
| 135 | 350.3 | 3.331 | 321.7 | 869.9 | 1191.6. | 135 |
| 140 | 353.1 | 3.219 | 324.6 | 867.6 | 1192.2 | 140 |
| 145 | 355.8 | 3.112 | 327.4 | 865.4 | 1192.8 | 145 |
| 150 | 358.5 | 3.012 | 330.2 | 863.2 | 1193.4 | 150 |
| 155 | 361.0 | 2.920 | 332.9 | 861.0 | 1194.0 | 155 |
| 160 | 363.6 | 2.834 | 335.6 | 858.8 | 1194.5 | 160 |
| 165 | 366.0 | 2.753 | 338.2 | 856.8 | 1195.0 | 165 |
| 170 | 368.5 | 2.675 | 340.7 | 854.7 | 1195.4 | 170 |
| 175 | 370.8 | 2.602 | 343.2 | 852.7 | 1195.9 | 175 |
| 180 | 373.1 | 2.533 | 345.6 | 850.8 | 1196.4 | 180 |
| 185 | 375.4 | 2.468 | 348.0 | 848.8 | 1196.8 | 185 |
| 190 | 377.6 | 2.406 | 350.4 | 846.9 | 1197.3 | 190 |
| 195 | 379.8 | 2.346 | 352.7 | 845.0 | 1197.7 | 195 |
| 200 | 381.9 | 2.290 | 354.9 | 843.2 | 1198.1 | 200 |
| 205 | 384.0 | 2.237 | 357.1 | 841.4 | 1198.5 | 205 |
| 210 | 386.0 | 2.187 | 359.2 | 839.6 | 1198.8 | 210 |
| 215 | 388.0 | 2.138 | 361.4 | 837.9 | 1199.2 | 215 |
| 220 | 389.9 | 2.091 | 363.4 | 836.2 | 1199.6 | 220 |
| 225 | 391.9 | 2.046 | 365.5 | 834.4 | 1199.9 | 225 |
| 230 | 393.8 | 2.004 | 367.5 | 832.8 | 1200.2 | 230 |
| 235 | 395.6 | 1.964 | 369.4 | 831.1 | 1200.6 | 235 |
| 240 | 397.4 | 1.924 | 371.4 | 829.5 | 1200.9 | 240 |
| 245 | 399.3 | 1.887 | 373.3 | 827.9 | 1201.2 | 245 |
| 250 | 401.1 | 1.850 | 375.2 | 826.3 | 1201.5 | 250 |
| 260 | 404.5 | 1.782 | 378.9 | 823.1 | 1202.1 | 260 |
| 270 | 407.9 | 1.718 | 382.5 | 820.1 | 1202.6 | 270 |
| 280 | 411.2 | 1.658 | 386.0 | 817.1 | 1203.1 | 280 |
| 290 | 414.4 | 1.602 | 389.4 | 814.2 | 1203.6 | 290 |
| 300 | 417.5 | 1.551 | 392.7 | 811.3 | 1204.1 | 300 |
| 350 | 431.9 | 1.334 | 408.2 | 797.8 | 1206.1 | 350 |
| 400 | 444.8 | 1.17 | 422.0 | 786.0 | 1208.0 | 400 |
| 450 | 456.5 | 1.04 | 435.0 | 774.0 | 1209.0 | 450 |
| 500 | 467.3 | 0.93 | 448.0 | 762.0 | 1210.0 | 500 |
| 600 | 486.6 | 0.76 | 469.0 | 741.0 | 1210.0 | 600 |

TABLE 2. — PROPERTIES OF SATURATED STEAM FOR VARYING AMOUNTS OF VACUUM
Calculated from Marks and Davis Tables

| Vacuum Height Inches | Absolute Pressure Pounds | Temperature Degrees Fahrenheit | Heat of the Liquid Above 32 Degrees B.t.u. | Latent Heat Above 32 Degrees B.t.u. | Total Heat Above 32 Degrees B.t.u. | Density or Weight per Cubic Foot Pound |
|---|---|---|---|---|---|---|
| 29.5 | .207 | 54.1 | 22.18 | 1061.0 | 1083.2 | 0.000678 |
| 29 | .452 | 76.6 | 44.64 | 1048.7 | 1093.3 | 0.001415 |
| 28.5 | .698 | 90.1 | 58.09 | 1041.1 | 1099.2 | 0.002137 |
| 28 | .944 | 99.9 | 67.87 | 1035.6 | 1103.5 | 0.002843 |
| 27 | 1.44 | 112.5 | 80.4 | 1028.6 | 1109.0 | 0.00421 |
| 26 | 1.93 | 124.5 | 92.3 | 1022.0 | 1114.3 | 0.00577 |
| 25 | 2.42 | 132.6 | 100.5 | 1017.3 | 1117.8 | 0.00689 |
| 24 | 2.91 | 140.1 | 108.0 | 1013.1 | 1121.1 | 0.00821 |
| 22 | 3.89 | 151.7 | 119.6 | 1006.4 | 1126.0 | 0.01078 |
| 20 | 4.87 | 161.1 | 128.9 | 1001.0 | 1129.9 | 0.01331 |
| 18 | 5.86 | 168.9 | 136.8 | 996.4 | 1133.2 | 0.01581 |
| 16 | 6.84 | 175.8 | 143.6 | 992.4 | 1136.0 | 0.01827 |
| 14 | 7.82 | 181.8 | 149.7 | 988.8 | 1138.5 | 0.02070 |
| 12 | 8.80 | 187.2 | 155.1 | 985.6 | 1140.7 | 0.02312 |
| 10 | 9.79 | 192.2 | 160.1 | 982.6 | 1142.7 | 0.02554 |
| 5 | 12.24 | 202.9 | 170.8 | 976.0 | 1146.8 | 0.03148 |

# INDEX